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Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

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Each table is designated by a six-digit number, the first two of which refer to the type of reaction, the third to the phase of the homogeneous reaction, gaseous (1), liquid (2), or solid (3). The indication of the phase is repeated at the upper right-hand corner of the first sheet of each table. The second three-digit group of the table number refers to the types of substances involved. Within each table, reactions are numbered. In tables including more than one page, the table number is repeated at the head of each page, and the pages are numbered. Each table starts on a new sheet.

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Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

National Bureau of Standards

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SUPPLEMENT 3 TO TABLES OF CHEMICAL KINETICS HOMOGENEOUS REACTIONS

PREFACE

A description of these Tables and definition of the terms and abbreviations used may be found in the introduction to the 1951 publication. A brief description of the method used in compiling these tables and the limitation of coverage is given in the preface to Supplement 1. A description of the numbering system used in classifying reactions for the tables is given in Supplement 2. The present supplement contains information pertaining to Substitution, Exchange and Elimination reaction types. It is not complete as still more material falling in these groups is being prepared. The amount of kinetic data to be studied made it seem advisable to present all the material completed to date without further delay. The date on each section gives the year and month to which the literature had been surveyed. Significant omissions or errors should be reported to Dr. Charles H. Stauffer, Head, Department of Chemistry, St. Lawrence University, Canton, New York.

The Director and his associates gratefully acknowledge the financial assistance provided by the Office of Ordnance Research, Department of the Army which made this work possible. The Director of the Project gratefully acknowledges the able assistance of his associates and collaborators, the help of the National Bureau of Standards, the National Academy of Sciences and the members of the Committee on Chemical Kinetics of N.R.C. Division of Chemistry.

C.H. Stauffer

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ISOTOPIC EXCHANGE

Hydrogen exchange on aliphatic C

Gas phase

Amounts are in M/l. Rate constants are in M/l and sec. Rates are in gram atoms/l and sec.

R listed under mass action law indicates quantity listed under k is rate of reaction not rate constant.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C_2H_4 + D_2 \longrightarrow C_2H_3D, C_2H_5D, C_2H_4D_2, C_2H_6, H_2, HD$	$A = B \simeq 1.8 \times 10^{-3}$	$dL/dt = R$	569	2.4	-7				*	([2])
	(A) (B) (L) (M) (N) (O) (P) (Q)			598	5.8	-7					
				616	1.22	-6					
				643	4.0	-6					
				662	6.4	-6	57				
			$dM/dt = R$	569	1.6	-7					
				598	3.9	-7					
				616	4.7	-7					
				643	8.9	-7					
				662	1.3	-6	35				
			$dQ/dt = R$	569	1.0	-7					
				598	2.7	-7					
				616	5.4	-7					
				643	1.8	-6					
				662	3.4	-6	61				
			$-dA/dt = R$	569	4.1	-7					
				598	1.3	-6					
				616	2.0	-6					
				643	4.7	-6					
				662	9.9	-6	52				
.2	$C_2H_5Br + DBr \longrightarrow C_2H_4DBr + HBr$	$10^3A = 2\text{-}24$; $10^3B = 1\text{-}12$	$k\,AB$	258	7.2	-10				*	([1])
				306	1.7	-8	40	2	7		

COMMENTS

Reaction: (.1) Selected data. Complex chain reaction involves both exchange and addition. Authors list 14 reactions as contributing to mechanism. Determined rates of formation of all six products listed and both reactants. Units converted from molecules $cc.^{-1}$ min^{-1}. (.2) Data erratic and results give only order of magnitude. Reaction partially heterogeneous, air and Br_2 accelerate exchange and Hg inhibits exchange.

LITERATURE

(1) J.B. Peri, F. Daniels, *ACS* 1950, **72**, 424. (2) R.E. Varnerin, J.S. Dooling, *ACS* 1956, **78**, 1119.

ISOTOPE EXCHANGE
Oxides of carbon

Gas phase

Amounts are in M/l unless stated otherwise.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Isotopic tracer	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	$C^*O_2 + CO \longrightarrow CO_2 + C^*O$	$10^3A = 1\text{-}12$	C^{14}			$k\,A^{0.85}B^{0.73}$	799	1.2	-4		*	(2)
		$10^3B = 1\text{-}8$					850	5.6	-4			
			C^{13}				867	5.0	-4			(1)
							898	8.3	-4			
			C^{14}				900	2.6	-3	77		(2)
			C^{13}				917	1.3	-3			(1)
				Argon	0-0.008		850	5.6	-4			(2)
				N_2	0.0005		850	1.2	-3			
					0.0003		900	4.6	-3			

COMMENTS

Reference. (1) Used mass-spectrometric method with enriched C^{13} or O^{18} to follow exchange. Results of (1) recalculated by (2) to fit empirical rate law of (2). Definite heterogeneous catalysis observed by (1) with quartz or gold surface, also catalysis by H_2O or H_2 with concentration ~0.0002 increasing rate by a factor of five. (2) Increased S/V ratio

COMMENTS *(continued)*

by factor of 6 using packed quartz vessel with almost negligible effect, but still concluded reaction to be predominantly heterogeneous because of the erratic nature of results. Both observed normal first order exchange rate (McKay rate law) and chemical kinetic rate law obtained from variation of exchange rate with concentrations of reactants.

LITERATURE

(1) J.D. Brandner, H.C. Urey, *J.C.P.* 1945, **13**, 351.

(2) T.H. Norris, S. Ruben, *J.C.P.* 1950, **18**, 1595.

ISOTOPIC EXCHANGE
Halogen on aliphatic-C

Gas phase

Amounts are in M/l. Rate constants are in M/l and sec. Rates are in gram atoms/l and sec.

kF_X in mass action law column indicates quantity listed under k is pseudo first order rate constant for isotopic equilibration.
R in mass action law column indicates quantity listed under k is rate of isotope exchange in gram atoms per liter sec ([4]).

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C^{14}O + COCl_2 \longrightarrow CO + C^{14}OCl_2$	10^4A=1-8; 10^4B=2-20	Cl_2	0.003-0.016	$kA^{\frac{1}{2}}B^{\frac{1}{2}}[Cl_2]$	375	2.0	-3				*	([7])
						400	5.7	-3					
						420	1.5	-2					
						450	4.6	-2	39.3	4	10		
.2	$CH_3Cl + HCl^* \longrightarrow CH_3Cl^* + HCl$	10^3A=1.3-6; 10^3B=1.3-6	pyrex glass	S/V=7.4 cm^{-1}	kA	375	2.2	-6				*	([1])
						390	4.8	-6					
						405	1.1	-5					
						420	2.4	-5					
						435	4.4	-5					
						450	8.2	-5					
						465	1.67	-4	43.6	1.4	9		
.3	$CH_3I + I_2^* \longrightarrow CH_3I^* + II^*$	$10^2A \sim 2$; $10^4B \sim 3$			$kAB^{\frac{1}{2}}$	185	3	-4				*	([2])
						250	4	-3					
						375	6	-1	>32				
.4	$CH_2FCl + HCl^* \longrightarrow CH_2FCl^* + HCl$	10^3A=1-6; 10^3B=1-6	pyrex glass	S/V=7.4 cm^{-1}	kA	420	1.55	-6				*	([1])
						450	8.2	-6					
						480	2.6	-5					
						510	8.9	-5	47.1	1.4	9		

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.5	$CHF_2Cl + HCl^* \longrightarrow CHF_2Cl^* + HCl$	$10^3A=1.3-6$; $10^3B=1.3-6$	pyrex glass	S/V=4-1800 cm^{-1}	$kA^{\frac{1}{2}}B^{\frac{1}{2}}$	360	2.8	-6				*	(1)
						375	5.3	-6					
						405	1.47	-5					
						420	2.5	-5					
						465	8.7	-5	30.2	9	4		
.6	$CF_3Cl + HCl^* \longrightarrow CF_3Cl^* + HCl$	$A \sim 10^{-3}$; $B \sim 10^{-3}$			kF_X	405	< 2	-7				*	(1)
						510	7	-7					
.7	$Cl_3CBr + Br_2^* \longrightarrow Cl_3CBr^* + BrBr^*$	$10^2A=1-4$; $10^3B=3-17$			$kAB^{\frac{1}{2}}$	146	2.97	-5				*	(3)
						159	9.63	-5					
						172	3.03	-4					(8)
						183	7.26	-4	33.1	5.6	12		
		$10^3A=4-20$; $10^4B=3-5$			$kAB^{\frac{1}{2}}$	150	7.2	-5					
						170	3.1	-4					
						200	2.9	-3					
						220	9.5	-3	29				
			O_2, H_2O, Cl_2	0.00006 / 0.00016	(see comments)								
.8	$Cl_3CBr + Br^* \longrightarrow Cl_3CBr^* + Br$	$10^2A=1-4$; $10^3[Br_2]=3-17$			kAB	146-183			10.3	7.9	10	*	(3)
									7				(8)
.9	$C_2H_5Br + HBr^* \longrightarrow C_2H_5Br^* + HBr$	$10^3A=2-16$; $10^6B=3-2000$	S/V=	1 cm^2/cm^3	kA	200	4.0	-7				*	(6)
				2		200	5.8	-6					
			air	150 mm.		200	7.0	-7					
			S/V =	1 cm^2/cm^3		243	3.0	-6					
						254	1.3	-5	32				
.10	$C_2H_5Br + DBr^* \longrightarrow C_2H_5Br^* + DBr$	$10^3A=8$; $10^3B \sim 3$				258	6	-6				*	(6)
		$10^3A=2$; $10^3B=1-4$				306	2	-4					
.11	$(CH_3)_3CCl^* + SnCl_4$	not stated			kAB	25	2	-1	>3			*	(3)

COMMENTS

General. Exchange follows general first order rate law (McKay). Chemical kinetic order of exchange reactions determined from variation of exchange rate with concentrations of reactants ([4]).

Reaction: (.1) Rate law calculated by editor from half times and concentrations of reactants. Listed because of excellent agreement of sixteen out of seventeen separate values at 400°C. (.2) Reaction predominantly heterogeneous as rate constant found to be linear with respect to surface to volume ratio, S/V, from 3 to 14 cm^{-1} with straight line going through origin. Activity of surface increased with use but reproducibility obtained by baking and evacuating. (.3) Reaction predominantly heterogeneous even at highest temperature in pyrex bulb of 1 l. capacity. Packed reaction vessel gave straight line plot of log k vs. T^{-1}. Activation energy 17 kcals. for heterogeneous reaction and >32 kcals. for homogeneous reaction estimated from slope of log k vs. T^{-1} plot at highest T in unpacked flask. (.4) Reaction predominantly heterogeneous as rate constant found to be linear with respect to surface to volume ratio, S/V, from 3 to 14 cm^{-1} with straight line going through origin. Activity of surface increased with use, but reproducibility obtained by baking and evacuating. (.5) Reaction homogeneous as calculated rate constants independent of surface to volume ratio, S/V=4-1800 cm^{-1}. (.6) Pseudo first order rate constant for isotopic equilibration gives order of magnitude only. (.7) Reaction homogeneous as proved by increasing S/V ratio by factor of 12. Quartz and Pyrex vessels gave identical results. Addition of O_2, H_2O, and Cl_2 in amounts indicated had no effect. Both ([3]) and ([8]) consider reaction to involve rapid equilibrium $Br_2^* \rightleftarrows 2Br^*$ followed by rate determining step (.8). (.8) Calculated from (.7) and equilibrium constant for reaction forming bromine atoms. Addition of HBr at [HBr] =0.038 results in parallel formation of Cl_3CH to extent of about 20% of A at half time of exchange. (.9)(.10) Reaction heterogeneous as increase of S/V ratio by factor of 6 increased rate of exchange 200 times. Coating surface with "Drifilm" had no effect. Coating walls with black decomposition product decreased rate and gave reproducible results, but did not change activation energy. (.10) Parallel H-D exchange about four orders of ten slower. See 301.401. (.11) Reaction partially heterogeneous as glass packing increased exchange rate several fold. Authors also observed less than 1% exchange in 6 hrs. at 200°C for $SnCl_4$ with CH_3Cl, $C_2H_5(CH_3)CHCl$, CH_3CCl_3 and CCl_4.

LITERATURE

(1) J.E. Boggs, L.O. Brockway, *ACS* 1955, **77**, 3444. (2) D. Clark, H.O. Pritchard, A.F. Trotman-Dickenson, *CSL* **1954**, 2633. (3) N. Davidson, J.H. Sullivan, *J.C.P.* 1949, **17**, 176. (4) G.M. Harris, *TFS* 1951, **47**, 716. (5) R.A. Howald, J.E. Willard, *ACS* 1955, **77**, 2046. (6) J.B. Peri, F. Daniels, *ACS* 1950, **72**, 424. (7) D.R. Stranks, *TFS* 1955, **51**, 524. (8) J. Willard, A. Miller, *JCP* 1949, **17**, 168.

ISOTOPIC EXCHANGE
Halogen in IVth group halide

Gas phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	$\Delta S^{\ddagger}$
.1	$SiCl_4 + HCl^{36} \longrightarrow SiCl_3Cl^{36} + HCl$	10^2A=1-5; 10^2B=1-2	kA^2B	90	2.7	-2				
		2.5 1-6		100	6.1	-2				
		2.2 0.7		108	9	-2	22	1.1	9	-18

COMMENTS

Rate constant of exchange reaction calculated from half time of isotopic equilibration and concentration of A+L and B+M. Order with respect to A found to be 1.9 ± 0.1 and B 0.95 ± .05. Authors found no effect upon rate of reaction by a threefold change in S/V or by strong illumination.

LITERATURE

R.H. Herber, *J.C.P.* 1957, **27**, 653.

ISOTOPIC EXCHANGE
Oxides of Nitrogen

Gas phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$NO + N^{15}O_2 \rightarrow N^{15}O + NO_2$	A+B = 0.0018				-35	>1	3				*	([2])
.2	$N^{15}O_2 + N_2O_5 \rightarrow NO_2 + N^{15}NO_5$	10^3A=1.5-2; 10^4B=7-10			kB	-9	1.9	-3				*	([1])
		2-3 15-20				0	5.2	-3					
			CO_2	0-.03		0	5.2	-3					
		1-2 30	NO	0.002		0	1.6	-2					
		3-4 30-50		0		10	1.4	-2	16	3	10		

COMMENTS

Reaction: (.1) Rate law not verified value gives only lower limit. (.2) Change of surface volume ratio has no effect on rate in absence of NO.

LITERATURE

([1]) A.R. Amell, F. Daniels, *ACS* 1952, **74**, 6210. ([2]) E. Leifer, *JCP* 1940, **8**, 301.

ISOTOPIC EXCHANGE
Hydrogen-hydrogen halide

Gas Phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
				k^o	n		A^o	n
.1	$D_2 + HCl \longrightarrow HD + DCl$	kAB	492	2.0	-3			
			511	5.3	-3			
			533	1.34	-2			
			553	2.9	-2			
			570	9.4	-2	53	3	15

COMMENTS

Homogeneous reaction accompanied by small amount of heterogeneous reaction, correction for which has been made. Unit converted from M/cc and temperatures from °K. Authors assume Arrhenius constant A to have $T^{1/2}$ dependence and consequently give $E = 52.1$ and $A = 6.3 \times 10^{10} T^{1/2}$.

LITERATURE

P. Cross, H. Steiner, *JCP*, 1936, **4**, 165.

ISOTOPIC EXCHANGE
Halogen-halogen halide

Gas phase

Amounts are in M/l. Rate constants are in M/l and sec. Rates are in gram atoms/l. and sec.

R listed under mass action law indicates quantity listed is rate of isotope exchange see ([3]).

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$ClF_3 + F_2^{18}$	10^4A=3-120; 10^3B=8-36	kA	194	1.57	-5				*	([1])
				224	5.0	-5					
				257	4.2	-4	29	4	8		
.2	$BrF_5 + F_2^{18}$	10^4A=5.1; 10^3B=6.32	R	193	8.5	-7				*	([1])
		14.7 6.32		193	8.0	-7					
		29.6 6.32		193	6.7	-7					
		55.2 6.32		193	5.6	-7					
		55.1 16.4		193	1.15	-6					
		55.1 35.6		193	2.25	-6					
		4.0 4.62		224	3.0	-6					
		12.5 4.62		224	3.7	-6					
		44.9 4.62		224	2.25	-6					
		84.5 4.62		224	2.12	-6					
		44.8 15.5		224	7.2	-6					
		44.8 32.6		224	1.38	-5					
		5.0 3.98		256	1.20	-5					
		15.0 3.98		256	9.8	-6					
		35.0 3.98		256	9.0	-6					
		86 3.98		256	7.2	-6					
		34.9 32.1		256	7.3	-5					

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
					k^o	n		A^o	n		
.3	$IF_7 + F_2^{18}$	10^3A=3-11; 10^2B=1.4-3		181	2.7	-5				*	(1)
		1.4-20 0.3-3		194	3.3	-4					
		4-17 0.4-2.5		224	3.5	-3	40	1	15		

COMMENTS

General: For general treatment of isotope exchange reactions see (3). In cases where the rate constant for the chemical process responsible for exchange has not been explicitly determined the quantity listed under k will be the rate of isotope exchange, R, in gram atoms per liter per second. This is indicated by listing "R" in the "Defined mass action law column":

$$R = -\frac{m \cdot n \cdot \underline{A} \cdot \underline{B}}{(m \cdot \underline{A} + n \cdot \underline{B})\, t} \ln(1-x)$$

where m and n are the number of exchangeable atoms of the labeled species in A and B respectively. $\underline{A}$ represents the sum of [A] + [L] and $\underline{B}$ represents the sum of [B] + [M]. X is the fractional extent of isotopic equilibration having taken place at time t.

Reaction: (.1) Authors consider exchange is simultaneously taking place by a heterogeneous and a homogeneous reaction and have separated the total rate of exchange into these two parts. Values listed are for the assumed homogeneous reaction. Rate of the heterogeneous reaction, is given by $R_{het.} = k_{het.} xByA/(1+xB+yA)^2$, where x and y represent adsorption coefficients of B and A respectively at the nickel halide surface of the nickel reaction vessel. Authors list $10^4 k_{het.} x$ as 4.5, 18 and 85 at 194, 224 and 257°C respectively with $E_{het.}$=24. Addition of H_2F_2 had no effect on exchange rate. Preliminary experiments by (2) indicated reaction about 10 times faster in aluminum reaction vessel. (.2) Exchange considered to be principally heterogeneous with rate law given by:

$$R = k_{het.} xByA/(1+xB+yA)^2$$

where x and y represent adsorption coefficients of B and A respectively at the nickel halide surface of the nickel reaction vessel. Authors list $10^4 k_{het.} x$=5.5, 37 and 125 at 193, 224 and 256°C respectively with $E_{het.}$=23. Preliminary studies by (2) showed no effect by NiF_2. (.3) Exchange considered to consist of simultaneous homogeneous and heterogeneous reaction at nickel halide surface of nickel reactor. Values listed are for the assumed homogeneous reaction. Rate of the heterogeneous reaction is expressed by $R_{het.} = k_{het.} xByA/(1+xB+yA)^2$, where x and y represent adsorption coefficients of B and A respectively at the reaction vessel surface. Authors list $10^4 k_{het.} x$ as 4.5, 6.2 and 25 at 181, 194 and 224°C. respectively with $E_{het.}$=18.5.

LITERATURE

(1) R.M. Adams, R.B. Bernstein, J.J. Katz, *J.C.P.* 1954, **22**, 13. (2) R.B. Bernstein, J.J. Katz, *J.P.C.* 1952, **56**, 885. (3) G.M. Harris, *TFS* 1951, **47**, 716.

ISOTOPIC EXCHANGE

Ammonia(ammine) complex on Group Ielement

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.
Time of fractional exchange in seconds.

No.	Reaction	Solvent	Amount of reactant	% exchange	Time	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$Cu(N^{15}H_3)_4^{++} + NH_3$	NH_3	$10^3A = 6$	100	180		-33				(2)
.2	$Ag(N^{15}H_3)_2^{+} + NH_3$	NH_3	$10^2A = 2$	99.6	30		-33				(2)
.3	$CuKe_2 + Cu^{*++} \longrightarrow Cu^{*}Ke_2 + Cu^{++}$ (copper II salicylaldehydeethylenediimine)	pyridine	$10^3A = 10^3B = 1.5\text{-}15$			kAB	25	2.6	-3	*	(1)

COMMENTS

(.3) Rate law with respect to A and B individually not verified as A = B in all experiments.

LITERATURE

(1) R.B. Duffield, M. Calvin, *ACS* 1946, **68**, 557. (2) H.U.D. Wiesendanger, W.H. Jones, C.S. Garner, *JCP* 1957, **27**, 668.

ISOTOPIC EXCHANGE

Halogen complex on group I element

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$AuCl_4^- + 4Cl^{*-} \longrightarrow AuCl_4^{*-} + 4Cl^-$	H_2O	10^3A = 3-12; 10^3B = 8-76	HCl NaCl	0.003-.012 μ=0.088	$k_1A + k_2AB$	0 0 10 10 0	k_1 3.3 k_1 1.83 k_2 4.5 k_2 5.4 k_2 2.5	-3 -1 -3 -1 -1	4 16	8 2	2 14
					μ = 0.248							

COMMENTS

(.1) Value of k_2 calculated at μ = 0.248 on basis of assumed no change for k_1 with ionic strength.

LITERATURE

R.L. Rich, H. Taube, *JPC* 1954, **58**, 1.

ISOTOPIC EXCHANGE
Valence states group I ion

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$Ag^{*+} + Ag^{+2} \longrightarrow Ag^{+} + Ag^{*+2}$	H_2O	$10^3(A+B)$=5-16; A/B=5-17	$HClO_4$	5.87	kB^2	-15	3.0	+2			
			3-31 2-25		5.87		0	1.02	+3			
			5-8 5-20		4.9		0	1.8	+3			
			10 20		4.4		0	3.1	+3			
			8 20-30		3.94		0	4.9	+3			
			4-18 5-20		5.87		11	2.74	+3	12.5	1.1	13

COMMENTS

In the limited range studied reaction appears to follow inverse fourth order with respect to H^+. Mechanism of exchange probably involves a rapid equilibrium of the type $2Ag^{+2} \rightleftharpoons Ag^{+} + Ag^{+3}$.

LITERATURE

B.M. Gordon, A.C. Wahl, *ACS* 1958, **80**, 273.

ISOTOPIC EXCHANGE

Cyanide complex group II element

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$Zn(CN)_4^{-2} + C^{14}N^-$	H_2O	A = B = 0.025	KOH	pH = 10.3		25	very fast					*	(1)
.2	$HgCN^+ + Hg^{*+} \longrightarrow Hg^*CN^+ + Hg^+$	H_2O	10^3A=2-16; 10^3B=6-49	HNO_3	pH=2.4-2.8	kAB	0	7	-3				*	(1) (2)
			7 2		μ=0.12		9	1.6	-2					
							17	3.5	-2					
							25	6	-2					
							30	9	-2	14	1	9		
.3	$HgCN^+ + Hg^{*2+} \longrightarrow Hg^*CN^+ + Hg^{2+}$	H_2O	10^3A=6-34; 10^4B=6-200	$NaClO_4$, $HClO_4$	pH=1.5-2.8	kAB	0	1.7	-2				*	(2)
					μ=0.02-.12		13	4.9	-2					
							20	9.2	-2	13	6	8		
						k^*AB	0	1.3	-2					
							13	3.4	-2					
							20	6.0	-2	12	4	7		

COMMENTS

Reaction: **(.1)** Complete exchange within 120 seconds. **(.2)** In absence of CN^- exchange is immeasurably fast. Rate constant calculated by (2) from rate data of (1). No effect on rate observable by authors of pH=0.85-2.7, ionic strength= 0.1-2., O_2=0.1-760 mm of Hg. or colloidal Hg. **(.3)** Rate constant listed as k is observed value calculated from pseudo first order exchange rate and concentrations of A and B. Rate constant listed as k^* is value of constant corrected by authors for apparent exchange caused by the disproportionation reaction $2HgCN^+ \rightleftharpoons Hg^{++} + Hg(CN)_2$.

LITERATURE

(1) A.C. MacDiarmid, N.F. Hall, *ACS* 1954, **76**, 4222.
(2) R.L. Wolfgang, R.W. Dodson, *JPC* 1952, **56**, 872.
(3) R.L. Wolfgang, R.W. Dodson, *ACS* 1954, **76**, 2004.

ISOTOPIC EXCHANGE
Valence states Group III ions

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec. Coded solvents at end of table.

Concentrations in gross concentration of all forms unless indicated otherwise.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$Ce^{*+3} + Ce^{+4} \longrightarrow Ce^{+3} + Ce^{*+4}$	H_2O	$10^3A = 2\text{-}18$; $10^3B = 2\text{-}17$	HNO_3	6.00	$k\,AB$	-14	1.28	-2					(15)
			$\mu = 6.18$		1.00		-10	6.9	-2				*	(12)
					2.01		-10	3.0	-2					
					1.00		- 6	1.16	-1					
					1.00		0	3.2	-1					(12) (4)
					2.01		0	9.8	-2					(12)
					2.42		0	7.5	-2					
					3.68		0	4.2	-2					
					6.18		0	3.7	-2					(11) (12) (15)
					6.18		25	2.9	-1	12	1	8		
				HNO_3	6.00									
				KF	0.00013		-14	1.11	-1					(15)
					0.00025		-14	2.3	-1					
					0.00047		-14	4.2	-1					
					0.00063		-14	5.0	-1					
					0.00080		-14	6.7	-1					
					0.00080		0	1.02	0					
			$10^3A = 1\text{-}9$; $10^3B = 1\text{-}10$	H_2SO_4	0.4	$k\,AB$	0	4.2	-1					(5) (27)
			0.5 0.5				10	1.16	-1					(27)
			0.8-8 1-10	$HClO_4$	6.0	$k\,AB + k'\,AB^2$	0	k 5	-2					(10)
							0	k' 9.3	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$Ce^{*+3} + Ce^{+4} \longrightarrow$ *(continued)*	H_2O	$10^3A = 0.8-8$; $10^3B = 1-10$	$HClO_4$	5.85	$kAB + k'AB^2$	0	k 9.3					*	(10)
							0	k' 9.8						
					5.04		0	k 1.5	-1					
							0	k' 1.44	+1					
					3.97		0	k 4.8	-1					
					3.00		0	k 7.0	-1					
					2.04		0	k 1.12	0					
		H_2O	$10^3A = 2-20$; $10^3B = 2-42$	$HClO_4$	6.18	$k_1A + k_2AB$	0	k_1 8	-5				*	(12)
							0	k_2 6.7	-3					
							10	k_1 3	-4	19	3	11		
							10	k_2 1.9	-2	17	2	11		
.2	$Eu^{*+2} + Eu^{+3} \longrightarrow Eu^{+2} + Eu^{*+3}$	H_2O	$10^2A = 3-7$; $10^2B = 3-12$	H^+	0.1-1.6	$kAB[Cl^-]$	32	8.2	-4				*	(21)
				Cl^-	0.1-2		39	1.80	-3					(20) (21)
				$NaClO_4$	$\mu = 2.0$		50	5.3	-3	21	6	11		(21)
.3	$Tl^{*+1} + Tl^{+3} \longrightarrow Tl^{+1} + Tl^{*+3}$	H_2O	$10^2A = 10^2B = 2.44$	HNO_3	1.0	kAB	25	1.6	-3				*	(23)
					1.5		25	2.3	-3					
			$10^4A = 8-85$; $10^4B = 8-34$	H_2SO_4	1.6		0	2.25	-3					(5)
					1.6		25	1.98	-2					
					2.2		25	1.3	-2					(3)
					1.6		44	7.7	-2	14	3	8		(5)
			$10^2A = 10^2B = 1.0$	$H_2SO_4 = 1.60$;	$Na_2SO_4 = 0.39$		25	1.60	-2					(3)
			$\mu = 3.68$		1.28	0.57	25	1.80	-2					
					0.85	0.80	25	2.33	-2					
					0.65	0.95	25	2.92	-2					
			$10^2A = 10^2B = 1.0$	$H_2SO_4 = 0.0$	$HClO_4 = 3.12$		24	6.4	-5					(30)
					0.006	3.11	24	1.0	-4					
					0.015	3.10	24	1.6	-4					
					0.030	3.09	24	2.6	-4					

Supplement 1959

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.3	$Tl^{*+1} + Tl^{+3} \longrightarrow$ *(continued)*	H_2O	$10^2A = 10^2B = 1.0$	H_2SO_4 =	0.047; $HClO_4$ =	3.07 k AB	24	3.5	-4				*	([30])
					0.093	3.03	24	7.4	-4					
					0.158	2.96	24	1.1	-3					
					0	3.12	37	1.8	-4					
					0.015	3.10	37	4.4	-4					
					0.030	3.09	37	7.0	-4					
					0.047	3.07	37	9.7	-4					
					0.093	3.03	37	1.7	-3					
					0.158	2.96	37	2.9	-3					
					0.49	2.63	37	1.05	-2					
		H_2O	$10^2A = 10^2B = 1.0$	H_2SO_4 =	0 ; $NaClO_4$ =	3.12 k AB	50	5.0	-4	15	1	7		
			"		0.047	3.07	50	2.7	-3	15	4	7		
			"		0.093	3.03	50	4.8	-3	14	1	7		
			"		0.158	2.96	50	5.3	-3	12	4	5		
			$10^2A \simeq 1.0$; $10^2B = 1.08$	H_2SO_4 =	2.19; HCl =	0.0010	25	1.18	-2					([3])
			" "			.0030	25	1.03	-2					
			" "			.0050	25	6.8	-3					
			" "			.0080	25	3.7	-3					
			" "			.010	25	2.2	-3					
			" 1.15			.014	25	8.2	-4					
			" "			.017	25	2.3	-4					
			" "			.02-.03	25	3.6	-5					
			" 1.08			.04	25	6.7	-5					
			0.5 0.65			.025	25	6.8	-5					
			1.0 1.08			.049	25	9.8	-5					
			0.5 0.65			.030	25	1.07	-4					
			" "			.035	25	1.55	-4					
			" "			.062	25	5.7	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.3	$Tl^{*+1} + Tl^{+3} \longrightarrow$ *(continued)*	H_2O	$10^2A \lesssim 2.5$; $10^2B \lesssim 2.5$	$HClO_4$	0.8-3.5	k AB;	10	k_1 8.9	-6				*	(24)
				$NaNO_3$	0-0.4	$k = k_1 + k_2[H^+]^{-1} + k_3[NO_3^-]$	10	k_2 6.4	-6					
					μ=3.68		10	k_2 1.05	-4					
							25	k_1 4.3	-5					
							25	k_2 1.9	-5					
							25	k_3 4.4	-4					
							37	k_1 1.41	-4					
							37	k_2 4.2	-5					
							37	k_3 1.30	-3					
							50	k_1 4.5	-4	18	4	8		
							50	k_2 6.7	-5	10	9	2		
							50	k_3 3.6	-3	16	2	8		
			10^4A=1-250; 10^4B=1-170	$HClO_4$ =	0.3	k AB	25	2.12	-5					(14)
				$+NaClO_4$	1.0		25	1.94	-5					
				μ = 6.0	2.0		25	1.83	-5					
					4.0		25	1.19	-5					
					6.0		25	8.7	-6					
					0.3		32	3.86	-5					
					1.0		32	3.64	-5					
					2.0		32	3.25	-5					
					4.0		32	2.67	-5					
					6.0		32	1.93	-5					
					0.3		42	8.8	-5					
					1.0		42	8.4	-5					
					2.0		42	7.8	-5					
					4.0		42	6.0	-5					
					6.0		42	5.1	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.3	$Tl^{*+1} + Tl^{+3} \longrightarrow$ *(continued)*	H_2O	$10^2A = 3$; $10^3B = 4$	$HClO_4$ =	0.5	kAB	50	2.06	-4				*	(9)
				$+NaClO_4$	1.0		50	1.83	-4					
				$\mu = 6.0$	2.0		50	1.58	-4					
					4.0		50	1.19	-4					
					6.0		50	1.05	-4					
				$\mu = 4.0$	0.5		50	5.54	-4					
					1.0		50	4.34	-4					
					2.0		50	4.06	-4					
					4.0		50	3.92	-4					(9) (13)
				$\mu = 2.0$	0.5		50	6.7	-4					(9)
					1.0		50	8.1	-4					
					2.0		50	8.1	-4					
				$\mu = 1.0$	0.5		50	7.4	-4					
					1.0		50	8.7	-4					(9) (13)
				$\mu = 0.5$	0.5		50	7.4	-4					
			$10^4A = 1-250$; $10^4B = 1-170$	$HClO_4$	6.0	kAB	32	1.93	-5					(14)
				$+NaCl$ =	0.01		32	<6	-9					
					0.02		32	1.7	-8					
					0.06		32	3	-6					
					0.12		32	3.0	-5					
					0.20		32	9.7	-5					
					0.40		32	7.6	-4					
					1.00		32	6.4	-3					
					1.50		32	9.6	-3					
					0.40		42	3.6	-3					
					1.50		42	3.1	-2					
			$10^3A = 5-50$; $10^3B = 5-50$	$HClO_4$	3.50									
				$+CH_3COOH$ =	0.005		25	3.6	-5					(2)
					0.010		25	3.5	-5					
					0.020		25	3.2	-5					
					0.050		25	2.6	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.3	$Tl^{*+1} + Tl^{+3} \longrightarrow$ *(continued)*	H_2O	$10^3A = 5-50$; $10^3B = 5-50$	$HClO_4$	3.50	kAB							*	(2)
				$+ (CH_2COOH)_2$	= 0.003		25	3.4	-5					
					0.010		25	3.4	-5					
					0.020		25	3.1	-5					
					0.050		25	1.7	-5					
				$HClO_4$	0.5									
				$+ HCN =$	0		30	2.1	-4					(22)
					0.1 × B		30	1.7	-4					
					0.5 × B		30	1.0	-4					
					1.0 × B		30	4.6	-5					
					1.7 × B		30	3.0	-6					
					2.5 × B		30	2.2	-6					
					3 × B		30	1.0	-6					
				NaCN	17 × B		30	5.8	-5					
					26 × B		30	2.0	-4					
					34 × B		30	4.7	-4					
					44 × B		30	1.2	-3					
					68 × B		30	5.1	-3					
					85 × B		30	1.3	-2					
.4	$U^{+4} + U^{*+6} \longrightarrow U^{*+4} + U^{+6}$	H_2O	$10^2A = 2.0$; $10^2B = 2.0$	H_2SO_4	1.91	kAB	30	3	-6				*	(1)
			$10^2A = 3-6$; $10^2B = 2.7$	HCl, NaCl	pH = 0.85	kA^2B	25	5.0	-3					(18) (25)
			2.5 2-15	$NaClO_4$	0-1		25	3.2	-3					
		Et 30*	$10^2A = 1-3$; $10^2B = 1.5-3$	HCl	0.0326	kAB	25	2.1	-2					(19)
			2 2-4		0.0651		25	6.9	-3					
			2 2		0.130		25	2.0	-3					
		Et 60*	2 3		0.0326	kAB	25	5.0	-2					
			2 3		0.0651		25	2.3	-2					
			1-3 2-4		0.130		25	1.33	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$U^{+4} + U^{*+6} \longrightarrow$ *(continued)*	Et 90*	$10^2A = 1.7$; $10^2B = 2.1$	HCl	0.186	kA^3	25	2.5	0				*	(19)
			0.8-2.4 1-2.8		0.252		25	1.86	0					
			1.7 2.1		0.314		25	1.4	0					
		C_2H_5OH	0.67 0.69		0.0078	kB^3	25	2.3	+1					
			1.3 1.4		0.039		25	7.0	0					
			1-2 1.4-2.8		0.077		25	2.1	0					
			1.3 1.4		0.116		25	1.6	0					
.5	$Np^{+4} + Np^{*+5} \longrightarrow Np^{*+4} + Np^{+5}$	H_2O	$10^3A = 4-100$; $10^3B = 5-50$	$HClO_4$, $NaClO_4$	$[H^+] = .04-.3$	$kA^{3/2}B^{\frac{1}{2}}[H^+]^{-2}$	25	6.4	-8				*	(28)
					$\mu = 0.8-1.7$		47	5.0	-6	37	6	19		
			4-30 13-50		$[H^+] = .5-1$	$kB^2[H^+]$	25	1.1	-5					
					$\mu = 1.2$		47	9.8	-5	18	1	8		
					1.7		47	1.6	-4					
					2.1		47	2.1	-4					
					3.0		47	3.3	-4					
.6	$Np^{*+5} + Np^{+6} \longrightarrow Np^{+5} + Np^{*+6}$	H_2O	$10^5A = 10^5B = 1.5$	$HClO_4$	0.106	kAB	0	2.1	+1				*	(6)
			$10^5A = 3-10$; $10^5B = 2-9$		0.3-1.0, $\mu = 1$		0	3.0	+1					(7)
			$10^5A = 10^5B = 2$	HNO_3	0.99		0	3.1	+1					(8)
					3.00		0	8.9	+1					
				HNO_3	0.99									
					$\mu = 1.6$		0	3.6	+1					
					2.3		0	4.6	+1					
					2.9		0	7.0	+1					
					4.2		0	1.21	+2					
		H_2O	$10^5A = 10^5B = 2$	$HClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $La(ClO_4)_3$	$[H^+] = 0.1-3$, $\mu = 3.0$	kAB; $k = k_1 + k_2[H^+]$	0	$k_1 5$	+1					(29)
							0	$k_2 1$	+1					
							5	$k_1 7.4$	+1	12	2	11		
							5	$k_2 1.5$	+1	15	1	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6	$Np^{*+5} + Np^{+6} \longrightarrow$ *(continued)*	H_2O	$10^5A=3-10$; $10^5B=2-9$	$HClO_4$, $NaClO_4$	$[H^+]=0.3-1$, $\mu = 1.0$	kAB	10	5.1	+1	8	1	8	*	(7)
			$10^5A=10^5B=2$	$[H^+] = 3$	$\mu = 3$									(8)
				$Cl^- =$	0.10		0	1.07	+2					
					0.23		0	1.19	+2					
					0.55		0	1.32	+2					
					1.37		0	1.52	+2					
					1.5-2.7		0	1.6	+2					
					0.21		5	1.75	+2					
					0.55		5	1.92	+2					
					1.37		5	2.4	+2					
					0.21		10	2.4	+2					
					0.55		10	2.9	+2					
					1.37		10	4.0	+2					
		D_2O	$10^5A = 10^5B = 2$	$NaClO_4$, $DClO_4 =$	$\mu = 3.0$	kAB								
					0.1		5	5.4	+1					
					1.0		5	6.6	+1					
					3.0		5	9.8	+1					
.7	$Pu^{*+3} + Pu^{+4} \longrightarrow Pu^{+3} + Pu^{*+4}$	H_2O	$10^6A=3-23$; $10^6B=4-22$	$HClO_4$, $LiClO_4$	0.4-2, $\mu=2.0$	$k_1AB + k_2A[PuOH^{+3}]$	0	$k_1 2$	+2				*	(16) (17)
							0	$k_2 1.3$	+4					
							12	$k_1 4$	+2					(16)
							12	$k_2 1.2$	+4					
							25	$k_1 2$	+1	8	3	8		
							25	$k_2 2.0$	+4	3	2	6		

CODED SOLVENTS

Et 30* (60) (90) C_2H_5OH vol. % indicated + H_2O

COMMENTS

Reaction: (.1) Rate constants calculated on basis of first order dependence with respect to each reactant although log plot indicated order with respect to B to be 0.9 ± .05. Rate constants calculated from data of ([15]) in half times. ([12]) observe that plot of rate constant vs. $[H^+]^{-2}$ is linear. ([15]) observe that plot of rate versus [KF] is linear. ([10]) concludes that data conforms to rate law $R=k_1[Ce^{+3}][Ce(OH)_3^+] + k_2(Ce^{+3})(HOCeOCe^{+5})$. Values of k_1 and k_2 are not given. In range B = 0.0009 to 0.010 ([10]) finds plot of $RA^{-1}B^{-1}$ linear with respect to B and concludes reaction is best expressed by the combined second and third order rate law given. In range B=0.002-0.04 ([12]) finds plot of RA^{-1} linear with respect to B but straight line does not go through the origin. ([12]) therefore concludes reaction is best expressed by the combined first and second order rate law given. (.2) Variation of $[H^+]$ from 0.1 to 1.56 caused change in calculated k of only 1.60×10^{-3} to 1.82×10^{-3} at 39°C. (.3) Data of ([23]) calculated for rate law determined by later investigators. ([5]) observed slight catalysis of exchange by platinum foil, and also studied x-ray induced exchange. Selected data of ([3]). Dependence of calculated second order constant upon $[H^+]$ not completely determined. ([14]) ([24]) ([26]) express $k=k_o+k'[H^+]^{-1}$ based upon parallel exchange occurring with Tl^{+3} and $Tl(OH)^{+2}$ ions as exchanging species with Tl^{+1}. In contrast ([9]) uses $k^{-1}=k'+k''[H^+]$ based upon the assumption $Tl(OH)^{+2}$ is the only exchanging species. Plots of k vs. $[H^+]^{-1}$ and also k^{-1} vs. $[H^+]$ show some curvature for all data collected. Tables are therefore composed principally of the of the second order rate constants based upon total concentrations of the reacting species, as determined by the various investigators, with concentrations of acids and added salts given. Selected data for reasons of conservation of space. Ions such as Cl^- and CN^- both reduce exchange rate at low concentration and increase rate at higher concentrations. (.4) Exchange observed by ([1]) to be about 20 times faster when illuminated by 300 watt lamp 4cm. from reaction flask than in dark. Value listed is for reaction in dark. Activation energy of light reaction

COMMENTS *(continued)*

8 kcals. ([25]) observed no effect of light in presence of HCl and a negligible salt effect. Exchange rate proportional to $[H^+]^{-3}$ in the pH range 0.85 to 1.6 in H_2O as solvent. In mixed ethanol-water solvent ([19]) observed wide variation of order with solvent composition. Log-log plots gave best fit for the order 0.93 for A, 1.11 for B and -1.74 for HCl in 30 vol. % C_2H_5OH; 0.87 for A, 1.08 for B and -0.97 for HCl in 60 vol. % C_2H_5OH; 2.89 for A, 0.10 for B and -1.06 for HCl in 90 vol. % C_2H_5OH; and 0.0 for A, 2.70 for B and -1.26 for HCl in pure C_2H_5OH. ([19]) proposes rate expression is $k'[UOH^{+3}]^2[UO_2OH^+]$ and calculate k' from the expression:

$$R = k' \frac{A^2B}{\left(\frac{[H^+]}{3.4\times10^{-5}} + 1\right)^2 \left(\frac{[H^+]}{1.3\times10^{-5}} + 1\right)}$$

derived from the hydrolysis constants, $3.4\times10^{-5} = [UOH^{+3}][H^+]/[U^{+4}]$ and $1.3\times10^{-5} = [UO_2OH^+][H^+]/[UO_2^{++}]$. No definite trends in the calculated k' in any one solvent system although values vary by as much as a factor of two in both the 30 and the 60 vol. % ethanol. Agreement between values of calculated k' is better in the other solvents. (.5) At $[H^+]$ less than 0.3 exchange reaction appears to be independent of ionic strength or glass or platinum surfaces. At $[H^+]$ greater than 0.5 exchange reaction shows positive dependence upon ionic strength and some catalysis by platinum foil, gold foil and pyrex helices. At both the higher and lower acidities the exchange reaction is faster than the oxidation-reduction disproportionation reaction. (.6) Reaction found to be essentially independent of dielectric constant of solvent in range from 68 to 88.3 using ethylene glycol or sucrose with H_2O. At constant ionic strength exchange appears independent of $[H^+]$ up to HNO_3=2.0. This is possibly due to slight retarding effect observed for nitrate ion ([8]) balancing slight positive H^+ effect ([29]). Below μ=3.0 exchange rate is observed to be independent of positive ion Na^+, Mg^{++} or La^{+++}. At μ>3, ([29]) shows that effect of $Na^+ > Mg^{++} > La^{+++}$. ([8]) study catalysis by Cl^- at constant $[H^+]$ and ionic strength. They suggest two reaction schemes:
$R = k_o(NpO_2^+)(NpO_2^{++}) + k_1(NpO_2^+)(NpO_2Cl^+)$ or
$R = k_o(NpO_2^+)(NpO_2^{++}) + k_1(NpO_2^+)(NpO_2Cl^+) + k_2(NpO_2^+)(NpO_2Cl_2)$ and calculate the values of k_o, k_1 and k_2 according to each scheme. Data does not appreciably differentiate between these two rate expressions. (.7) Slight positive dependence upon ionic strength in range 0.7 to 2. Values probably give little more than order of magnitude because of difficulties of measuring such a rapid exchange.

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ISOTOPE EXCHANGE
H-D,(T) exchange on aliphatic C

Liquid phase

Amounts are in M/l. Rate constants are in gram atoms/l and sec.
Coded solvents at end of table.

kF_E under rate law indicates rate constant is for measured pseudo first order rate of isotope equilibration.

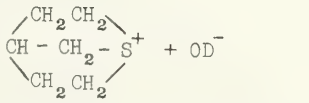
No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.11		$(CH_3)_2CHCH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B			kF_E	44	1.1	-5				*	(10)
.12		d-$C_2H_5CH(CH_3)CH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B			kF_E	60	1.0	-5				*	(10)
.13		n-$C_8H_{18} + D_2SO_4$	A	A sat. with B			kF_E	60	2.7	-8				*	(10)
.14		d-$C_2H_5CH(CH_3)CH_2CH_2CH_2CH_3 + C_2H_5SO_3D$	A	A sat. with B			kF_E	104	4	-7				*	(10)
.15		$C_2H_5CH(CH_3)CH_2CH_2CH_2CH_3 + ClSO_3D$	A	A sat. with B			kF_E	-78 -50	2 6	-6 -6					(10)
.16		$(CH_3)_3CCH_2CH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B			kF_E	60	5	-9				*	(10)
.17		d-$C_2H_5CH(CH_3)(CH_2)_7CH_3 + D_2SO_4$	A	A sat. with B			kF_E	60	4	-6					(10)
		Unsaturated Hydrocarbons													
.18		$HC{:}CH + D_2O$	B	B sat. with A	phosphate buffer	pH=8.6 9.0	kA	25 25	2.6 6.0	-3 -3				*	(1)
.19		$C_6H_5C{:}CD + H_2O$	B	B sat. with A acetate buffer phosphate buffer	HCl =.04 =.02 .02	.01 pH=5.0 7.0 7.9	kA	25 25 25 25	0 2 7.1 5.1	 -6 -5 -4				*	(1)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.19		$C_6H_5C{:}CD + H_2O$ *(continued)*	B	B sat. with A	phosphate buffer=	pH = .02 8.6	kA	25	1.3	-3				*	(1)
						.05 8.6		25	1.5	-3					
					borate buffer=	.014 9.0		25	4.6	-3					
						.012 9.5		25	1.2	-2					
						7-9.5	$kA[OH^-]$	25	4.6	+2					
.20		$C_6H_5C{:}CH + OH^- \longrightarrow C_6H_5C{:}C^- + H_2O$	C_5H_5N	A=0.4-1.4; 10^4B=1-100 M=5	$(CH_3)_4N^+$	= B	kAB	25	3.4	+3				*	(8)
		Ketones													
.21	.3	$CH_3COCH_3 + DOH \longrightarrow CH_3COCH_2D + H_2O$	A+M	2 vol. (A+L); 1 vol. (B+M)	K_2CO_3	.001	kAB	35	3.1	-5				*	(11)
						.003		35	7.8	-5					
						.01		35	9.0	-5					
						.03		35	1.09	-4					
						.01		40	1.47	-4	18	5	8		
.22		$CH_3COCH_2D + H_2O \longrightarrow CH_3COCH_3 + DOH$	B+L	2 vol. (A+L); 1 vol. (B+M)	K_2CO_3	.001	kAB	35	1.25	-5				*	(11)
						.003		35	3.1	-5					
						.01		35	3.6	-5					
						.03		35	4.3	-5					
						.01		40	5.8	-5	19	7	8		
.23		*dl*-$C_6H_5C{:}OCD(C_6H_5)CH_2CH(CH_3)_2 + H_2O$	8.4 D1*	A=0.1; $[CH_3COOH]=[CH_3COO^-]$		0.030	kA	98	5.7	-8				*	(21)
						0.050		98	9.8	-8					
						0.070		98	1.40	-7					
						0.100		98	2.05	-7					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.24		dl-$C_6H_5C{:}OCT(C_6H_5)CH_2CH(CH_3)_2 + H_2O$	8.4 D1*	A=0.1;	HCl	0.020	kA	98	5.2	-7				*	(21)
				μ=0.1		0.040		98	1.05	-6					
						0.060		98	1.61	-6					
					CH_3COOH	0.50		98	3.9	-9					
						0.75		98	5.6	-9					
						1.00		98	7.8	-9					
					CH_3COONa	0.01		98	1.12	-8					
						0.02		98	2.01	-8					
						0.06		98	6.1	-8					
						0.08		98	8.1	-8					
						0.10		98	1.03	-7					
					NaOH	0.0050		98	2.57	-5					
						0.0075		98	4.3	-5					
						0.010		98	6.4	-5					
					HCl	.02-.06	$kA[H^+]$	98	2.72	-5					
					CH_3COOH	0.5-1	$kA[CH_3COOH]$	98	7.7	-9					
					CH_3COONa	.01-0.1	$kA[CH_3COO^-]$	98	1.05	-6					
					NaOH	.005-.01	$kA[OH^-]$	98	7.7	-3					
		Carboxylic acid, (salt), (ester)													
.25		$HCOONa + D_2O$	B				kF_E	160	3.3	-7				*	(3)
								183	1.42	-6					
								214	1.29	-5	30	4	8		
.26		$DCOONa + H_2O$	B				kF_E	179	1.91	-6					(3)
								195	7.1	-6					
								208	1.72	-5	34	3	10		
.27	.5	$CH_3COOD + D_2O \longrightarrow CH_2DCOOD + DOH$	B				kF_E	~130	3	-7				*	(2)
								160	~2	-6					(4)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.28		$CH_3COO^- + D_2O \longrightarrow CH_2DCOO^- + DOH$	B		Na^+	= A	kF_E	150	1.1	-6				*	(18)
					Ca^{++}	= A/2		150	~1	-6					
					Ba^{++}	= A/2		150	~1	-6					
				A = 2.2	K^+	= A		160	~4	-6				*	(4)
.29		$(CH_3COO)_2Co + D_2O$	B	A sat.			kF_E	150	1.6	-6				*	(18)
.30		$(CH_3COO)_2Cd + D_2O$	B	A sat.			kF_E	150	3.2	-6				*	(18)
.31		$(CH_3COO)_2Hg + D_2O$	B	A sat.			kF_E	150	6	-6				*	(18)
.32		$(CH_3COO)_2Pb + D_2O$	B				kF_E	150	3	-5				*	(18)
.33		$CH_3CH_2COOD + D_2O \longrightarrow CH_3CHDCOOD + DOH$	B	A=7-12; B=15-25			kF_E	~130	6	-8				*	(2)
.34		$CH_3COOC_2H_5 + C_2H_5OD$	B	A ≃ 6	C_2H_5ONa	~0.2	kF_E	25	4.7	-6				*	(7)
.35		$CH_3CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	9	-7				*	(7)
.36		$CH_3CH_2CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	3.8	-7				*	(7)
.37		$(CH_3)_2CHCOOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	1.1	-7				*	(7)
.38		$(CH_3)_2CHCH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	1.3	-7				*	(7)
.39		$CH_2CH_2CH_2CH_2CH_2CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	3.2	-7				*	(7)
.40		$CH_3(CH_2)_9CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	3.8	-7				*	(7)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.41	$CH_3(CH_2)_{15}CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	3.1	-7				*	(7)
.42	$C_6H_5CH_2COOC_2H_5 + C_2H_5OD$	B	A ≃ 1	C_2H_5ONa	~0.2	kF_E	0	5.4	-3				*	(7)
.43	$C_6H_5(CH_3)CHCOOC_2H_5 + C_2H_5OD$	B	A ≃ 2	C_2H_5ONa	~0.2	kF_E	0	1.2	-3				*	(7)
.44	$(C_6H_5)_2CHCOOC_2H_5 + C_2H_5OD$	B	A ≃ 1	C_2H_5ONa	~0.2	kF_E	0	2.3	-3				*	(7)
	Hydroxy, (alkoxy)-substituted carboxylic acid, (salt), (ester)													
.45	$DOCH_2COOD + D_2O$	B	A ≃ 2.5			kF_E	160	5.8	-7				*	(6)
.46	$HOCD_2COOH + H_2O$	B	A ≃ 2.5			kF_E	160	4.1	-7				*	(6)
.47	$CH_3O(CH_3)CHCOOC_2H_5 + C_2H_5OD$	B	A ≃ 5	C_2H_5ONa	~0.2	kF_E	25	2.1	-7				*	(7)
.48	$CH_3O(C_6H_5)CHCOOC_2H_5 + C_2H_5OD$	B	A ≃ 1	C_2H_5ONa	~0.2	kF_E	0	1.6	-3				*	(7)
	NR_2-substituted carboxylic acid													
.49	$ND_2CH_2COOD + D_2O$	B				kF_E	140	4.9	-5					(5)
							150	8.3	-5					
							160	1.4	-4	18	2	5		
.50	$NH_2CD_2COOH + H_2O$	B				kF_E	140	2.2	-5					(5)
							150	3.8	-5					
							160	6.5	-5	19	4	5		
	Di-carboxylic acid ester													
.51	$(C_2H_5OOC)_2CH_2 + C_2H_5OD$	B	A ≃ 2	o-HOC_6H_4COONa	~.003	kF_E	25	1.1	-5				*	(7)
.52	$(C_2H_5OOC)_2CHCH_3 + C_2H_5OD$	B	A ≃ 2	o-HOC_6H_4COONa	~.003	kF_E	25	1.6	-6				*	(7)
.53	$(C_2H_5OOC)_2CHC_6H_5 + C_2H_5OD$	B	A ≃ 2	o-HOC_6H_4COONa	~.003	kF_E	25	2.1	-6				*	(7)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Tetra-alkyl ion of Vth group element													
.54	$(CH_3)_4N^+ + OD^-$	D_2O	A=0.3; B≃0.3	Na^+, I^-	=B, A	kAB	84	3.1	-9				*	(22)
							100	2.3	-8	33	6	11		
.55	$(CH_3)_4P^+ + OD^-$	D_2O	A=0.3; B=0.26-0.4	Na^+, I^-	=B, A	kAB	27	9.8	-6				*	(22)
							56	4.7	-4	26	1	14		
.56	$(CH_3)_4As^+ + OD^-$	D_2O	A=0.3; B≃0.3	Na^+, I^-	=B, A	kF_E	62	7.2	-6				*	(22)
.57	$(CH_3)_4Sb^+ + OD^-$	D_2O	A=0.3; B≃0.3	Na^+, I^-	=B, A	kF_E	62	7	-7				*	(22)
	Tri-alkyl ion of VIth group element													
.58	$(CH_3)_3S^+ + OD^-$	D_2O	A=0.3; B≃0.3	Na^+, I^-	=B, A	kAB	0	2.9	-6				*	(22)
							27	1.16	-4	22	2	12		
.59	$(CH_3)_3Se^+ + OD^-$	D_2O	A=0.3; B≃0.3	Na^+, I^-	=B, A	kF_E	62	1.3	-5				*	(22)
.60	$(CH_3)_3Te^+ + OD^-$	D_2O	A=0.15; B≃0.3	Na^+, I^-	=B, A	kF_E	62	4	-6				*	(22)
.61	 $+ OD^-$ (bicyclo [2.2.1] heptane-1-sulfonium ion)	D_2O	A=1; B=0.31	Na^+, I^-	=B, A	kF_E	56	3	-7				*	(22)
	Alkyl sulfinyl, (sulfonyl)													
.62	$(n\text{-}C_4H_9)_2SO + OD^-$	D_2O	A≃1; B=2.2	Na^+, I^-	=B, A	kF_E	56	1.0	-8				*	(22)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.63	$\overline{CH_2CH_2CH_2CH_2}CDSO_2C_6H_4CH_3\text{-}p + OH^-$	D150*	$10^2A \sim 5$; $B \sim 0.4$			kAB	50	1.67	-5				*	(23)
							60	5.2	-5					
							71	1.67	-4	24.4	5	11		
.64	$\overline{CH_2(CH_2)_4}CDSO_2C_6H_4CH_3\text{-}p + OH^-$	D150*	$10^2A \sim 5$; $B \sim 0.4$			kAB	40	2.18	-6				*	(23)
							50	1.11	-5					
							70	8.4	-5					
							79	2.2	-4	25	1	12		
	Alkyl halides													
.65	$CHCl_2F + OH^- \longrightarrow CCl_2F^- + H_2O$	H_2O	$10^2A=3$; $10^2B=3$	Na^+	$=B$	kAB	0	1.57	-4				*	(13)
							20	3.9	-3	25	2	16		
.66	$CDCl_2F + OH^- \longrightarrow CCl_2F^- + DOH$	H_2O	$10^2A=3$; $10^2B=3$	Na^+	$=B$	kAB	0	8.9	-5				*	(13)
							20	2.55	-3	26	1	17		
.67	$CDBrClF + OH^-$	H_2O	$10^2A \sim 1$; $10^2B=1.7$	Na^+	$=B$	kAB	0	2.10	-3				*	(14)
							15	2.27	-2	25	1	17		
.68	$CDBr_2F + OH^-$	H_2O	$10^2A \sim 2$	CH_3NH_2 / $CH_3NH_3ClO_4$	0.04 / 0.05	$kAB + k_1A[CH_3NH_2]$	0	k 2.07	-2				*	(15)
							0	k' 1.3	-5					
							25	k 7.3	-1	23	5	16		
.69	$CDI_2F + OH^-$	H_2O	$10^3A \sim 3$	CH_3NH_2 / $CH_3NH_3ClO_4$	0.112 / 0.096	$kAB + k'A[CH_3NH_2]$	0	k 5.07	-2				*	(15)
							0	k' 2.7	-5					
							20	k 8.2	-1	22	2	16		
							20	k' 6.7	-4	26	2	16		
.70	$CHCl_3 + OD^-$	D_2O	$10^2A=1.3$; $10^3B=3.1$	Na^+	$=B$	kAB	20	2.07	-1				*	(16)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.71	$CDCl_3 + OH^-$	H_2O	10^2A=1.3; 10^3B=3.1	Na^+	=B	kAB	0	4.7	-3				*	(16)
			41				0	5.0	-3					
			3.1	$NaClO_4$	.038		0	4.6	-3					
			3.1				20	1.02	-1					
			3.1				35	7.4	-1	24	8	16		
			buffer	CH_3NH_2 / CH_3NH_3Cl	.016 / .0012	$kAB + k'A[CH_3NH_2]$	35	k'3	-4					
.72	$CDBr_2Cl + OH^-$	H_2O	$10^2A \simeq 1$; buffer	NH_3 / NH_4ClO_4	.1-.2 / .15-.4	$kAB + k'A[NH_3]$	0	k 1.44	-1				*	(14)
							0	k'8	-7					
							35	k 1.38	+1	22	4	16		
							35	k'1.9	-4					
.73	$CDICl_2 + OH^-$	H_2O	$10^2A \simeq 1$; buffer	NH_3 / NH_4ClO_4	.1-.2 / .15-.4	$kAB + k'A[NH_3]$	0	k 2.75	-2				*	(14)
							0	k'4	-7					
							35	k 3.14	0	23	3	16		
							35	k'6.5	-5					
.74	$CDBr_3 + OH^-$	H_2O	$10^2A \simeq 1$; buffer	NH_3 / NH_4ClO_4	.1-.2 / .15-.4	$kAB + k'A[NH_3]$	0	k 5.8	-1				*	(14)
							0	k'1.3	-5					
							20	k 8.3	0					
							20	k'2.0	-4					
							35	k 4.7	+1	20.8	3	16		
							35	k'1.4	-3					
.75	$CDI_3 + OH^-$	H_2O	$10^5A \simeq 5$; buffer	NH_3 / NH_4ClO_4	.02-.05 / .02-.05	kAB	0	6.0	-1				*	(14)
							24	1.39	+1	21	3	16		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.76	*cis*-ClCH:CHCl + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	70	very fast					*	(19)
.77	*trans*-ClCH:CHCl + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	3	1.7	-7				*	(19)
.78	*cis*-BrCH:CHBr + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	25	1.8	-6				*	(19)
.79	*cis*-BrCD:CDBr + CH_3OH	B	A=0.25-.26	CH_3ONa	.006-.08	$kA[CH_3ONa]$	26 31	3.3 1.0	-3 -2				*	(19)
.80	*trans*-BrCH:CHBr + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	25	1.2	-6				*	(19)
.81	*cis*-ICH:CHI + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	25	< 2	-7				*	(19)
.82	*trans*-ICH:CHI + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	55	very fast					*	(19)
.83	BrCH:CBr_2 + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	25	1.9	-5				*	(19)
.84	C_6H_5CH:CHBr + D_2O	B	saturated 2 phases	CH_3ONa	1-2	kF_E	110	1.2	-7				*	(19)
.85	Cl_2C:CClH + OD^-	H_2O	A (sat.); B≃6	Na^+	= B	kF_E	~82	4	-6				*	(17)
.86	Cl_2C:CClD + OH^-	D_2O	A (sat.); B≃6	Na^+	= B	kF_E	~82	3	-6				*	(17)
.87	$C_{10}H_{16}$.HCl + DCl (camphene hydrochloride)	$CHCl_3$	A=0.15-0.17; B=.05-.1			kAB	0	1.5	-3				*	(20)
.88	β-$C_6H_6Cl_6$ + C_2H_5OD	B	$10^2A = 1.8$	$C_2H_5O^-$	0.07	$kA[C_2H_5O^-]$	44	~1	-6				*	(9)

CODED SOLVENTS

8.4 Di*	8.4 M dioxane in H_2O
Di 50*	50 vol. dioxane with 50 vol. of H_2O

COMMENTS

General: For general treatment of isotope exchange reactions see ([12]). In all cases where defined mass action law is given as kF_E the pseudo first order isotopic equilibration constant is given as the rate constant. This is calculated from the fractional exchange, X, at time, t, by using the equation $k = 1/t \ln(1-x)$. In cases where the reverse exchange is negligible due to a large excess of one isotopic species this might be equal to first order rate constant for the reaction but this is not verified unless exchange dependence on reactant concentration has been determined.

Reaction: (.11) Exchange rate constant calculated from only one fractional exchange time. (.12) Exchange rate constant an average of three fractional exchange times. (.13) Exchange rate constant calculated from only one fractional exchange time. (.14) Average of exchange rates at 102 and 104°C. (.16) Exchange rate constant calculated from only one fractional exchange time. (.18) Exchange rate corrected for amount of A in gas phase by multiplying observed exchange rate by ratio of total A to A in liquid phase. Exchange rate independent of rate of shaking under conditions used. Total buffer conc.=.02. (.19) Exchange rate corrected for amount of A in second liquid phase by multiplying observed exchange rate by ratio of total A to amount of A in aqueous phase. Exchange rate not dependent upon rate of shaking under conditions used. (.20) Rate constant for exchange calculated from nuclear magnetic resonance measurements. Effective relaxation time is dependent upon rate constant of exchange reaction. (.21)(.22) Approximate values of rate constants for forward and reverse reaction of first step in isotope exchange calculated from analysis of rate of exchange and equilibrium isotope distribution. Rate law with respect to A and B not verified as ratio of (A+L) to (B+M) kept constant. (.23) Pseudo first order exchange rate law not verified as concentration of A kept constant. Under same conditions rate is about one fifth of observed rate of racemization for H-substituted compound interpreted to indicate an H/D isotope effect about equal to 5. (.24) Pseudo first order rate law with respect to A not confirmed as concentration of A kept constant. Ratio of catalytic constants to the catalytic constants for racemization of H-substituted compound averages about 11 interpreted to indicate an H/T isotope effect about 11 compared to H/D effect of 5, see (.23). (.25) Partial conversion of salt to HCOOD had no effect on exchange rate. Excess DCl however accelerated exchange. (.27) Calculated from a half time of about 100 hrs. (.28)(.29)(.30)(.31)(.32) Calculated from time for half exchange in hours. (.33) Calculated from percent exchange per day. (.34) through (.48) Approximate value of pseudo first order exchange rate constant calculated from percent exchange at one time only. Exchange probably occurs only

COMMENTS *(continued)*

at α-hydrogen. (.51)(.52)(.53) Approximate values as pseudo first order exchange rate constant calculated from percent exchange at one time only. Exchange probably occurs only at α-hydrogen. (.54)(.55) Second order rate law not verified. Rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. (.56)(.57) Approximate value as pseudo first order exchange rate constant calculated from percent exchange at one time only. (.58) Rate law not verified. Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. (.59)(.60)(.61)(.62) Approximate value as pseudo first order exchange rate constant calculated from percent exchange at one time only. (.63)(.64) Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. Activation energy recalculated and corrected by reviewer. (.65)(.66) Rate constant listed is for first step in isotope exchange and hydrolysis reaction. Hydrolysis reaction yields as products, NaF, NaCl, HCOONa and CO. Constants are based upon an assumed mechanism and steady state approximation. (.67) Concurrent hydrolysis reaction also studied, see 212.471. Products of hydrolysis are NaBr, NaCl, NaF, HCOONa and CO. (.68) Simultaneous hydrolysis reaction causes change of OH^- concentration during exchange. Samples titrated prior to determining D content. For hydrolysis reaction see 212.471 listed by authors. (.69) Simultaneous hydrolysis reaction not as appreciable as in (.68) see 212.471. (.70)(.71)(.72)(.73)(.74)(.75) Simultaneous solvolysis reaction is slower than exchange. Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. Rate law with respect to A not verified. (.76) Complete in 20 hours. Authors estimate rate under similar conditions about that of (.78). (.77)(.78) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.79) Second order rate constant calculated by dividing pseudo first order equilibration constant by concentration of $[CH_3ONa]$. Approximate values as extinction coefficients for C-D and C-H assumed identical. Exchange rate falls off rapidly probably due to parallel elimination reaction. (.80)(.81) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.82) Complete in 20 hours. Authors estimate rate under similar conditions to be less than (.80). (.83)(.84) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.85)(.86) Simultaneous solvolysis reaction caused concentration of B to drop to half its initial value during exchange. Value of pseudo first order exchange rate constant calculated from time of half exchange in hours and should be interpreted as only giving a rough order of magnitude. (.87) Second order rate constant identical within experimental order to second order rate constant for exchange of radioactive chlorine isotope between A and B. (.88) Simultaneous elimination reaction about 150 times faster than isotope exchange see 422.471. Exchange constant listed for order of magnitude only.

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ISOTOPE EXCHANGE

H-D(T) exchange on aromatic C

Liquid phase

Amounts are in M/l unless otherwise indicated.
Rate constants are in M/l and sec.

The position of the substitution is indicated in parentheses after the arrow in those cases where it has been determined.

kF_A under rate law indicates rate constant is for measured first order rate of isotope equilibration.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$C_6H_5D + H^+ \longrightarrow$	H_2O-$HClO_4$	B=10.43	ClO_4^-	10.43	kF_A	25	2.82	-6				*	(19)
			11.01		11.01		25	1.75	-5					
			11.71		11.71		25	1.35	-4					
		H_2O-H_2SO_4	10^3A=8; wt % H_2SO_4											
			66.5			kF_A	25	2.68	-7				*	(4)
			68.7				25	5.75	-7					
			73.5				25	3.52	-6					
			75.8				25	1.15	-5					
			79.2				25	4.53	-5					
			83.2				25	3.45	-4					
.4.1	$C_6H_5T + H^+ \longrightarrow$	H_2O-H_2SO_4	A=sat.; wt % H_2SO_4 = 79.2			kF_A	25	2.9	-5				*	(4) (17)
.5	$C_6H_5D + NH_2^- \longrightarrow$	NH_3	A=0.25-0.6; B=0.6	K^+	=B	kA	~-33	~ 1	-7				*	(7)
.5.1	$C_6H_6 + ND_2^- \longrightarrow$	ND_3	B=0.06			kF_A	25	2	-4				*	(23)
			0.03				25	1.7	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6	$o\text{-}CH_3C_6H_4D + H^+ \longrightarrow$	$H_2O\text{-}H_2SO_4$	A=sat.; wt. % H_2SO_4 = 68.0			kF_A	25	3.56	-7				*	(6)
			81.8				25	3.4	-4					(17) (18)
		$H_2O\text{-}CF_3COOH$	Mole %: A = 24.6; CF_3COOH = 62.9; H_2O = 12.5			kF_A	70	6.0	-7					(15)
.6.1	$o\text{-}CH_3C_6H_4T + H^+ \longrightarrow$	$H_2O\text{-}H_2SO_4$	A=sat.; wt. % H_2SO_4 = 81.8			kF_A	25	1.8	-4				*	(18)
.7	$o\text{-}CH_3C_6H_4D + H^+ \longrightarrow$	NH_3	A=0.25-0.6; B=0.6	K^+	= B		~-33	(no measurable exchange in 10 hrs.)						(7)
.8	$m\text{-}CH_3C_6H_4D + H^+$	$H_2O\text{-}H_2SO_4$	10^3A = 2; wt. % H_2SO_4 = 68.0			kF_A	25	8.2	-7				*	(6)
			A = sat. 81.8				25	1.0	-5					(17) (18)
.8.1	$m\text{-}CH_3C_6H_4T + H^+$	$H_2O\text{-}H_2SO_4$	A = sat.; wt. % H_2SO_4 = 81.8			kF_A	25	6.0	-6				*	(18)
.9	$p\text{-}CH_3C_6H_4D + H^+$	$H_2O\text{-}H_2SO_4$	10^3A = 2; wt. % H_2SO_4 = 53.0			kF_A	25	1.36	-7				*	(6)
			58.5				25	9.4	-7					
			63.9				25	5.7	-6					
			68.9				25	5.0	-5					
			73.4				25	4.2	-4					
		$H_2O\text{-}CF_3COOH$	Mole % A = 24.2; CF_3COOH = 62.0; H_2O = 13.8				70	1.00	-6					(15)
			1.8 81.9 16.3				70	7.7	-6					(16)
.9.1	$p\text{-}CH_3C_6H_4T + H^+$	$H_2O\text{-}H_2SO_4$	A = sat.; wt. % H_2SO_4 = 81.8			kF_A	25	1.7	-4				*	(18)
.10	$C_6H_5CH_3 + T^+$ (o:m:p=47: 1: 41)	A	10^2B = 7	NO_2	.001-.002	$kB[NO_2]$	25	7	-4				*	(1) (17)
			2-7		.0002-.02		140	1.9	-2	10	4	3		
			2-14	$SnCl_4$	.007-0.5	$kB[SnCl_4]$	25	2.2	-4					
			7		0.07		140	4.4	-3	10	5	3		
.11	$p\text{-}(CH_3)_3CC_6H_4D + H^+$	$H_2O\text{-}CF_3COOH$	Mole % A = 1.8; CF_3COOH = 81.9; H_2O = 16.3			kF_A	70	8.2	-6				*	(16)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
	Phenols, phenolates and alkyl-phenyl ethers													
.12	$C_6H_5OH + D^+$	H_2O	$10^2A=2$; $10^3B=42$	Cl^-	= B	k AB	90	1.33	-7				*	(8)
			7.8				100	5.0	-8					
			23.5				100	2.00	-7					
			42				100	3.8	-7					
			83				100	9.0	-7					
			118				100	1.4	-6					
			167				100	2.3	-6					
			222				100	3.5	-6					
			7.8				110	1.5	-7					
			42				110	1.11	-6					
			7.8				120	3.67	-7	27.2	5	8		
			42				120	2.56	-6	27.4	4	9		
.13	$C_6H_5O^- + D^+$	H_2O		OH^-		k AB				24.8	8	9		(9)
.14	$2,6\text{-}D_2\text{-}4\text{-}CH_3C_6H_2OH + H^+$	$H_2O\text{-}H_2SO_4$	$10^2A=2.5$; wt. % $H_2SO_4=9.8$			k F_A	25	6.1	-8				*	(3) (5)
			14.5				25	1.73	-7					
			19.3				25	4.00	-7					
			27.0				25	1.33	-6					
			34.5				25	4.70	-6					
			45.3				25	4.38	-5					
		$H_2O\text{-}HCl$	$10^2A=2.5$; wt. % HCl= 7.10				25	3.95	-7					
			11.66				25	1.33	-6					
			15.16				25	3.89	-6					
			21.5				25	3.06	-5					
.15	$o\text{-}CH_3OC_6H_4D + H^+$	$H_2O\text{-}H_2SO_4$	$10^3A=3.5$;	H_2SO_4	5.18	k F_A	25	1.49	-6				*	(19)
					5.90		25	3.63	-6					
					6.82		25	1.21	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.15	o-$CH_3OC_6H_4D + H^+$ *(continued)*	H_2O-H_2SO_4	10^3A=3.5;	H_2SO_4	7.34	kF_A	25	2.91	-5				*	(19)
					7.88		25	5.2	-5					
		CH_3COOH	$A \simeq 0.1$	H_2SO_4	0.550		25	1.40	-6					
					1.23		25	5.10	-6					
					2.64		25	4.50	-5					
			$A \simeq 3$	H_2SO_4	$\simeq$0.3		80	2.9	-5					(14)
		(mole ratio	$CH_3COOH:A:H_2SO_4$ = 5:1:0.1)		$\simeq$0.3		100	1.5	-4	22	1	9		
.16	m-$CH_3OC_6H_4D + H^+$	H_2O-$HClO_4$	$10^2A \simeq 1.5$	$HClO_4$	10.04	kF_A	25	3.00	-7				*	(19)
					10.43		25	7.20	-7					
					11.01		25	3.24	-6					
					11.71		25	2.00	-5					
.17	p-$CH_3OC_6H_4D + H^+$	H_2O-H_2SO_4	10^3A=3.5	H_2SO_4	3.51	kF_A	25	2.93	-7				*	(19)
					4.86		25	1.85	-6					
					5.95		25	8.8	-6					
					6.77		25	2.55	-5					
					7.59		25	8.4	-5					
		CH_3COOH	$A \simeq 0.1$	H_2SO_4	0.232		25	5.0	-7					
					0.632		25	3.00	-6					
					0.916		25	5.0	-6					
					1.72		25	2.30	-5					
					2.68		25	8.2	-5					
					3.52		25	2.10	-4					
		CH_3COOH	$A \simeq 3$	H_2SO_4	$\simeq$0.3	kF_A	80	8.8	-5				*	(14)
		(mole ratio	$CH_3COOH:A:H_2SO_4$ = 5:1:0.1)		$\simeq$0.3		100	3.0	-4	16	7	5		
			$10^2A \simeq 8$	$ZnCl_2$	1.90		25	3.10	-7					(20)
					2.07		25	4.05	-7					
					2.68		25	8.2	-7					
					3.19		25	1.66	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	Defined mass-action law	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.17	p-$CH_3OC_6H_4D + H^+$ *(continued)*	CH_3COOH	$10^2A \simeq 8$; [HCl]=0.05	$ZnCl_2$	0.015	kF_A	25	3.24	-7				*	(20)
					0.040		25	5.8	-7					
					0.101		25	7.9	-7					
					0.220		25	7.2	-7					
					0.350		25	6.0	-7					
					0.650		25	3.71	-7					
			[HCl]=0.42	$ZnCl_2$	0.024		25	1.36	-6					
					0.048		25	2.19	-6					
					0.144		25	5.7	-6					
					0.290		25	1.05	-5					
					0.480		25	1.39	-5					
					1.12		25	1.77	-5					
					1.48		25	2.01	-5					
			$10^2A \simeq 8$	$SnCl_2$	0.059		25	3.01	-7					(22)
					0.118		25	7.1	-7					
					0.22		25	1.95	-6					
					0.596		25	6.3	-6					
					0.879		25	2.11	-5					
					2.90		25	1.59	-3					
			$10^2A \simeq 8$; [HCl]=0.115	$SnCl_2$	0.015		25	3.05	-7					
					0.147		25	2.98	-6					
					0.732		25	2.25	-5					
					1.10		25	6.2	-5					
.18	o-$CH_3OC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	=B	kF_A	~-33	1	-3					(7)
.19	m-$CH_3OC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	=B	kF_A	~-33	~1	-7					(7)
.20	p-$CH_3OC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	=B	kF_A	~-33	~1	-8					(7)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.21	p-$C_2H_5OC_6H_4D + H^+$	CH_3COOH	$A \simeq 2.5$	H_2SO_4	~0.25	kF_A	100	4.0	-4					(14)
.22	p-$CH_3CH_2CH_2OC_6H_4D + H^+$	CH_3COOH	$A \simeq 2.5$	H_2SO_4	~0.25	kF_A	100	4.0	-4					(14)
.23	p-$(CH_3)_2CHOC_6H_4D + H^+$	CH_3COOH	$A \simeq 2.5$	H_2SO_4	~0.25	kF_A	100	7.4	-4					(14)
.24	p-$C_6H_5OC_6H_4D + H^+$	CH_3COOH	not stated	H_2SO_4		kF_A	100	4.	-4				*	(14)
.25	$2,3,4$-$(CH_3O)_3C_6H_2T + H^+$	H_2O	$A < 0.04$	$KHSO_4$	0.50	kF_A	25	1.84	-7					(21)
					1.00		25	4.4	-7					
					2.00		25	1.05	-6					
					2.50		25	1.44	-6					
				$CHCl_2COOH$	0.12		25	3.4	-8					
					0.24		25	4.8	-8					
					1.21		25	1.51	-7					
					2.42		25	2.40	-7					
					4.84		25	6.0	-7					
					7.24		25	1.10	-6					
					12.13		25	1.23	-4					
				CF_3COOH	0.99		25	4.8	-7					
					2.16		25	1.22	-6					
					4.04		25	5.0	-6					
					6.73		25	1.37	-5					
.26	$2,4,6$-$(CH_3O)_3C_6H_2T + H^+$	H_2O	$10^5B = 1.3$ $[CH_3COOH] = [CH_3COONa]$ $\mu = 0.1$		0.01	kF_A	~25	2.3	-7				*	(13)
					0.025		~25	3.8	-7					
					0.05		~25	4.5	-7					
					0.1		~25	8.3	-7					
				strong acid	0.05		~25	4	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	N-substituted benzene (NH_2), ($NR'R''$), (NO_2)													
.27	$C_6H_5NH_3^+ + HDO$	HDO	A = 0.017			kF_A	79	2.14	-7				*	([12])
							90	6.7	-7					
							95	1.22	-6					
							100	2.24	-6	30	4	11		
.28	$2\text{-}OH\text{-}5\text{-}NO_2C_6H_2\text{-}1,3\text{-}D_2 + H^+$	H_2O	10^2A=1.9; wt. % H_2SO_4 =64.3			kF_A	25	1.16	-7				*	([3])
			70.3				25	4.40	-7					
			71.1				25	5.33	-7					
			78.8				25	4.85	-6					
			81.3				25	1.23	-5					
			82.9				25	2.70	-5					
			87.2				25	5.08	-5					
			92.2				25	1.01	-4					
			97.6				25	1.93	-4					
.29	$m\text{-}C_6H_4(NO_2)_2 + ND_3$	ND_3				kF_A	50	1.2	-6				*	([23])
.30	$p\text{-}C_6H_4(NO_2)_2 + ND_3$	ND_3				kF_A	50	3.7	-7				*	([23])
	Halogen-substituted Benzene													
.31	$2\text{-}FC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	> 4	-1				*	([7])
.32	$3\text{-}FC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	4	-4				*	([7])
.33	$4\text{-}FC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	2	-5				*	([7])
.34	$2\text{-}F_3CC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	6	-2				*	([7])

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.35	$3\text{-}F_3CC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	1	-3				*	(7)
.36	$4\text{-}F_3CC_6H_4D + NH_2^-$	NH_3	A=0.25-0.6; B=0.6	K^+	= B	kF_A	~-33	1	-3				*	(7)
.37	$2\text{-}HO\text{-}5\text{-}ClC_6H_2\text{-}1,3\text{-}D_2 + H^+$	H_2O	10^2A=2.1; wt. % H_2SO_4 =40.5			kF_A	25	1.57	-7				*	(3) (5)
			47.0				25	4.73	-7					
			53.0				25	1.59	-6					
			59.0				25	5.32	-6					
			63.5				25	1.59	-5					
			wt. % H_3PO_4 = 63.6				25	1.17	-7					
			68.1				25	2.67	-7					
			72.7				25	5.6	-7					
			76.4				25	1.48	-6					
	Anthracene													
.38	$9,10\text{-}D_2C_{14}H_8 + H^+$	H_2O	wt. % H_2SO_4 = 84.0	CCl_4	2 x vol.	kF_A	25	5.2	-4				*	(2)
			85.0				25	1.0	-3					
			85.9				25	1.7	-3					
			87.8				25	4.3	-3					
			90.0				25	2.3	-2					

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General: For general treatment of isotope exchange reactions see (8). In all cases where defined mass action law is given as kF_A the first order isotopic equilibration is given as the rate constant. This is calculated from the fractional exchange, X, at time, t, by the equation $k=-1/t\ ln(1-X)$. The rate constant for this may in special cases be a pseudo first order rate constant for the actual exchange reaction. For example this occurs if the reverse reaction is negligible due to an unlimited supply of one isotope from the solvent. It should be noted however that such a rate law has not been confirmed as being pseudo first order so long as dependence of exchange rate upon concentration of reactant has not been determined.

Reaction: (.4) First order rate constant only for isotopic equilibration, fractional exchange. (.4.1) Calculated first order constant for rate of isotopic equilibration from relative value of ([17]) combined with deuterium exchange rate of ([4]). (.5) Pseudo first order rate constant for reaction as written since reverse reaction eliminated by rapid exchange between NHD^- and solvent. (.5.1) First order rate constant only for isotopic equilibration, fractional exchange. (.6) Rate constant for first order isotopic equilibration only, value in 81.8 wt. % H_2SO_4 calculated from relative rate of ([17]) and rate for tritium exchange (.6.1) of ([18]). (.6.1) Rate constant for first order isotopic equilibration only, calculated from time vs. relative activity data of authors. (.8) Rate constant for first order isotopic equilibration only. Value for 81.8 wt. % H_2SO_4 calculated from relative rate ([17]) with rate for tritium exchange (.8.1) of ([18]). (.8.1) Rate constant for first order isotopic equilibration calculated from time vs. relative activity data of authors. Simultaneous sulfonation to extent of about 5% of the exchange observed. (.9) Rate constant for first order isotopic equilibration only. (.9.1) Rate constant for first order isotopic equilibration calculated from time vs. relative activity data of authors. (.10) Isomer distribution determined by ([17]) and kinetic data by ([1]). In absence of catalysts results erratic and first order rate constant estimated to be less than 10^{-6} sec.$^{-1}$ at 140°C. In presence of NO_2 as catalyst HCl was lost to extent of 1.5 to 2.3 times the amount of catalyst. No correction made for portion of reactants in vapor phase. The volume of vapor was from 5 to 10 times the volume of liquid. (.11) First order rate constant for isotopic equilibration. (.12) Rate law is for exchange of deuterium with ring hydrogen. Dependence of calculated rate constants upon hydrogen concentration of medium may be expressed at 100°C by:

$$\log k = 1.26 \log [H^+] - 4.68$$

or using an average activation energy of E = 27.3 the Arrhenius constant $A = 2.2 \times 10^{11} [H^+]^{1.26}$. (.14) First order rate constant for isotopic equilibration. Log k observed to be linear function of Hammett's acidity function $-H_o$ with slope of 1.08 in H_2SO_4 solution and slope of 1.42 in HCl solution. (.15) First order rate constant for isotopic equilibration. (.16) First order rate constant for isotopic equilibration for less than 25% reaction due to side reactions producing precipitate and dark coloration. It was impossible to obtain isotopic exchange data in H_2O-H_2SO_4 medium. (.17) First order rate constant for isotopic equilibration. (.24) Concentrations of reactants not stated but probably the same as (.21)(.22) and (.23). (.26) Temperature not stated but assumed to be room temperature. (.27) Rate data is only for exchange of ring hydrogen. (.28) Authors observe that log k is linear with Hammett's acidity function H_o with a slope = 0.94 up to about 85% H_2SO_4. Rate of sulfonation observed to be slow compared to exchange. (.29)(.30) Rate constants based on no more than one or two point determinations. (.31)(.32)(.33)(.34)(.35)(.36) Rate constant for isotope equilibration is pseudo first order rate constant for reaction as written since reverse reaction is negligible due to large excess of protons in

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solvent and rapid exchange between solvent and NH_2^-. (.37) Authors observe that log k is linear with Hammett's acidity function H_o with slope = 0.90 in H_2SO_4 and 1.00 in the H_3PO_4 solution. (.38) Reaction carried out in two phase system of 2 volumes of CCl_4 to 1 volume of acid solution. Concentration of A in CCl_4 layer = 0.1 M/l. Rate of stirring showed no appreciable effect. Initial rates are listed as rate of exchange increased with progress of reaction. Authors attribute this to increase in solubility of A in acid layer as parallel sulfonation proceeds.

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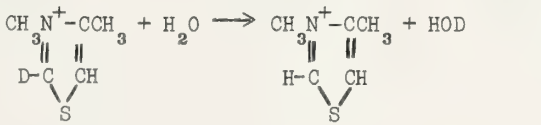
ISOTOPE EXCHANGE

H-D exchange on C in heterocyclic ring

Liquid phase

Amounts are in M/l. Rate constants are in gram atoms/l and sec., fractional times in sec.

kF_E under rate law indicates rate constant is for pseudo first order rate of isotope equilibration

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	pH	Defined mass-action law	Temperature	$t_{\frac{1}{2}}$	$k = k^o \times 10^n$ k^o	n
.1	 (3,4-dimethylthiozolium bromide)	H_2O	A = 1.1	Phosphate buffer, Br^-	0.02 = A	5.37	kF_E	~25	1,400	5	-4
.2	(3-benzyl-4-methylthiozolium bromide)	H_2O	A = 1.1	Phosphate buffer, Br^-	0.02 = A	5.37	kF_E	~25	450	1.5	-3

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Exchange followed spectrophotometrically in the infrared using O-D bond at 3.98μ and Beer's law followed in the region 20-80% transmittance.

LITERATURE

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ISOTOPIC EXCHANGE

Oxygen exchange on carbon

Liquid phase

Amounts are in M/l. Rates and rate constants are in gram atoms/l and sec. Coded solvents at end of table.

R under rate law indicates that constant listed is the rate of the chemical process responsible for exchange ([15]).

kF_E under rate law indicates that rate constant is for pseudo first order rate of isotopic equilibration.

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.2		$n\text{-}C_4H_9OH + H_2O^{18}$	B	A=0.73	H_2SO_4	0.046	kF_E	125	7	-8					([13])
						0.46			5.6	-7					
.3		$C_2H_5(CH_3)CHOH + H_2O^{18}$	B	A=0.8-1.6	$HClO_4$	0.111	kA	101	6.7	-7				*	([8])
						0.176		101	1.08	-6					
						0.284		101	3.2	-6					
						0.44		101	5.1	-6					
						0.70		101	8.6	-6					
						0.91		101	1.25	-5					
						1.15		100	1.09	-5					([9])
						2.35		100	3.4	-5					
						3.40		100	8.6	-5					
						4.10		100	1.34	-4					
.4		$(CH_3)_3COH + H_2O^{18}$	B	A=1.04	H_2SO_4	0.045	kF_E	55	1.33	-5					([13])
						0.45		55	1.54	-4					
						0.045		75	1.97	-4	30				
.5		$(CH_3)_3CCH_2OH + H_2O^{18}$	B	A=0.242	H_2SO_4	0.48	kA	125	1.4	-8					([12])

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6		$C_6H_5(CH_3)CHOH + H_2O^{18}$	B	not stated	$HClO_4$	.02-.08	$kA[H^+]$	30	1.07	-5				*	(14)
								54	3.3	-4	28	3	15		
.7		$(CH_3)_2C(OH)C(CH_3)_2OH + H_2O^{18}$	B	A~1	H_2SO_4	0.05	kF_E	73	9	-7					(7)
						1.6		73	6	-5					
						2.1		73	7	-5					
						5.35		73	5	-4					
.8		$4\text{-}CH_3OC_6H_4(C_6H_5)CHO^{18}H + H_2O$	D1 60*	A≃0.1; B≃22	$HClO_4$	0.101	kA	25	8	-5				*	(10)
						0.265		25	3.8	-4					
						0.394		25	7.5	-4					
						0.936		25	1.04	-3					
			D1 40*	A≃0.02; B≃33	$HClO_4$	0.35		25	1.2	-3					
						0.63		25	6.7	-3					
		Carbonyl oxygen													
.9		$CH_2OH(CHOH)_4CHO^{18} + H_2O$	B	A ≃1.1	buffers	pH=7.0	kF_E	40	1.0	-5				*	(17)
						7.0		50	2.8	-5					
						7.0		61	1.03	-4	23	2	11		
						8.1		61	2.3	-4					
						6.5		61	8.8	-5					
						6.0		61	4.4	-5					
						5.0		61	1.88	-5					
						3.4		61	1.92	-5					
						2.8		61	2.5	-5					
						2.1		61	1.05	-4					
						1.5		61	2.9	-4					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.10		$(CH_3)_2CO^{18} + H_2O$	A	B~5.5 salicylate buffer			kAB							*	(11)
				10^3[acid] = 1.97		10^3[salt] = 0.98		25	2.5	-6					
				1.99		9.92		25	2.4	-6					
				5.0		1.00		25	6.5	-6					
				10.4		1.01		25	1.35	-5					
Oxygen of carboxylic acid															
.11		$H_2C_2O_4 + H_2O^{18}$	B	10^3A=2.6-92	$HClO_4$	.002-1	$kA+k'A[H^+]$	25	k=1.23	-4				*	(16)
								25	k'=7.3	-4					
.12	.1	$C_6H_5CO^{18}OH + H_2O$	B	10^2A=5.6-10	HCl	0.09-0.5	$kA[H^+]$	80	2.4	-4				*	(18)
			Di 33*			0.07		80	1.6	-4					(5)
.13		p-$CH_3C_6H_4COOH + H_2O^{18}$	Di 33*	not stated	HCl	0.069	$kA[H^+]$	80	1.5	-4				*	(5)
.14		2,4,6-$(CH_3)_3C_6H_2COOH + H_2O^{18}$	Di 33*	not stated	HCl	0.069	$kA[H^+]$	80	1.5	-7				*	(5)
.15		p-$CH_3OC_6H_4COOH + H_2O^{18}$	Di 33*	not stated	HCl	0.064	$kA[H^+]$	80	1.00	-4				*	(5)
.16		m-$ClC_6H_4COOH + H_2O^{18}$	Di 33*	not stated	HCl	0.064	$kA[H^+]$	80	1.77	-4				*	(5)
.17		p-$ClC_6H_4COOH + H_2O^{18}$	Di 33*	not stated	HCl	0.064	$kA[H^+]$	80	1.1	-4				*	(5)
Oxygen of alkyl ester															
.18		$C_6H_5CO^{18}OC_2H_5 + H_2O$	B	10^3A=1-7	HCl	1.0	kA	99	7.5	-6				*	(1)
			Di 33*	10^2A=1		0.01	$kA[H^+]$	25	6.2	-8					(3)
.19		$C_6H_5CO^{18}OC_2H_5 + OH^-$	H_2O	$10^3A=10^3B$=1-7	Na^+	=B	kAB	25	6.3	-3				*	(1)
			Di 33*	$10^2A=10^2B$~1				9	1.8	-4					(3)
								25	7.8	-4					(1) (3)
								40	2.6	-3	14.9	6	7		(3)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.20		$C_6H_5CO^{18}OCH(CH_3)_2 + OH^-$	H_2O Di 33*	$10^3A=10^3B=1-7$	Na^+	= B	kAB	25 62	2.3 4.9	-3 -3				*	(1)
.21		$C_6H_5CO^{18}OC(CH_3)_3 + OH^-$	Di 33*	$10^3A=10^3B=1-7$	Na^+	= B	kAB	62	1.7	-4				*	(1)
.22		$C_6H_5CH_2CH_2CO^{18}OCH_3 + OH^-$	M 20*	$10^3A=10^3B\sim5$	Na^+	= B	kAB	25	1.46	-3				*	(4)
.23		$C_6H_5CH_2CH_2CO^{18}OC_2H_5 + OH^-$	M 30*	$10^3A=10^3B\sim5$	Na^+	= B	kAB	25	8.5	-4				*	(4)
.24		$2,4,6-(CH_3)_3C_6H_2COOCH_3 + H_2O^{18}$	Di 60*	$10^2A=2$			kA	126	1.5	-2				*	(2)
.25		$C_6H_5CH_2CHNH_2CO^{18}OC_2H_5 + H_2O$	B	$10^2A=1.5$	Cu^{++} buffer	0.0774 pH=7.3	kA	25	7	-4				*	(6)
.26		$C_6H_5CH_2CH(NHCOC_6H_5)CO^{18}OC_2H_5 + OH^-$	M 50*	$10^3A=10^3B\sim3$	Na^+	= B	kAB	25	3.0	-2				*	(4)
Oxygen of amide															
.27		$C_6H_5CO^{18}NH_2 + OH^-$	H_2O	A=B=0.1	Na^+	= B	kAB	41 80 109	7.6 1.87 1.26	-5 -3 -2	 17.5	 1.2	 8	*	(3)

CODED SOLVENTS

Di 33* (40), (60) Dioxane volume % indicated + H_2O

M 20* (30), (50) Methanol volume % indicated + H_2O

COMMENTS

General. For general treatment of isotope exchange reactions see ([15]). In all cases where defined mass action law is given as $k F_E$ the pseudo first order isotopic equilibration constant is given as the rate constant. This is calculated from the fractional exchange, X, at time, t, using the equation $k = -1/t \ln(1-x)$. In cases where the reverse exchange is negligible due to a large excess of one isotopic species this might be equal to a first order rate constant for the reaction but this is not verified unless exchange dependence on reactant concentration has been determined. In most cases where rate constant for the chemical process responsible for exchange has not been explicitly determined the value listed under k will be indicated in the "Defined mass action law" column by R, where R is the rate of the chemical process responsible for exchange, see ([15]).

Reaction. (.3) Selected values. ([8]) labeled oxygen in either A or B, also observed that racemization reaction twice as fast as exchange. ([9]) plotted log k vs. $-H_0$, Hammett's acidity function and obtained a straight line with slope of 1, at $[HClO_4] > 0.6$. (.6) Rate constant for exchange reaction about 20% smaller than rate con- for racemization reaction corrected for simultaneous elimination reaction. (.8) Rate law with respect to A not verified as [A] constant. Rate of exchange and rate of racemization essentially the same. (.9) Buffers used were barbituate, phosphate, acetate, phthalate, HCl-KCl, and oxalic acid. (.10) Selected data. Second order rate law not confirmed as concentrations of A and B not varied. Rate constant expressed by authors in terms of catalytic constants, $k = k_a[\text{acid}] + k_b[\text{base}] + k_H[H^+]$, where $k_a = 1.14 \times 10^{-3}$, $k_b = 2.5 \times 10^{-6}$, $k_H = 1.95$. Reaction found to be too sensitive to catalysis by both H^+ and OH^- to measure directly in absence of a buffer. (.11) Rate law calculated from only three observed points is based on calculated concentrations of species indicated not on total stoichiometric concentrations. (.12) Addition of 0.09 N KCl caused no significant change in rate. Either reactant labeled initially. (.13)(.14)(.15)(.16)(.17) Rate law with respect to H^+ not confirmed experimentally but assumed by ([5]). (.18) Rate constant calculated from pseudo first order rate constant of simultaneous hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. (.19)(.20)(.21)(.22)(.23) Rate constant calculated from second order rate constant of simultaneous alkaline hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. Authors use data to calculate rate constants for intermediate steps in their proposed mechanism of hydrolysis and exchange. (.24)(.25) Rate constant calculated from pseudo first order rate constant of simultaneous hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. (.26)(.27) Rate constant calculated from second order rate constant of simultaneous alkaline hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally.

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ISOTOPIC EXCHANGE

Sulfur exchange between disulfide and thiol

Liquid phase

Amounts are in M/l. Rate constants are in gram atoms/l and sec.
Coded solvents at end of table.

R under rate law indicates that constant listed is the rate of the chemical process responsible for exchange ([2])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$(n\text{-}C_4H_9S^*)_2 + n\text{-}C_4H_9SH$	BW6*	A = B = 0.01				25	$t_{\frac{1}{2}} = 2 \times 10^6$					*	([1])
			10^2A = 1.5-6;	NaOH	0.006	$kA[OH^-]$	0	3.8	-2					
			10^2B = 1-8				15	1.5	-1					
					.005-.01		25	3.1	-1					
							35	6.7	-1	14.1	7	9		
		MW12*	A = B = 0.0375	NaOH	0.0062	$kA[OH^-]$	0	2.9	-2					
							15	1.2	-1					
							25	2.6	-1					
							35	5.8	-1	14.4	1	10		
.2	$[(CH_3)_3CS^*]_2 + (CH_3)_3CSH$	MW12*	A = B = 0.061	NaOH	0.010	R	85	2.0	-7				*	([1])
							95	4.5	-7					
							100	6.7	-7					
							105	9.3	-7	22				
						$kA[(CH_3)_3CS^-]$	25	1	-7					
.3	$(n\text{-}C_6H_{13}S^*)_2 + n\text{-}C_6H_{13}SH$	MW12*	A = B = 0.0375	NaOH	0.0062	$kA[OH^-]$	25	2.6	-1					([1])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$(C_6H_5S^*)_2 + C_6H_5SH$	MW 12*	A = B = 0.0375	NaOH	0.0025	$kA[OH^-]$	0	4.6	-2					(1)
							15	2.0	-1					
							25	4.9	-1					
							35	1.3	0	15.8	2	11		

CODED SOLVENTS

BW6* n-$C_4H_9OH + H_2O$ (6%)

MW12* $CH_3OH + H_2O$ (12%)

COMMENTS

General: For general treatment of isotopic exchange reactions see (2).

Reaction: **(.1)** Rate law verified by variation of concentrations of A, B and NaOH. Rate constants calculated by dividing exchange rate, $R = -\frac{1}{t}\frac{A \times B}{A+B} ln(1-X)$, by A and [NaOH]. A and B represent concentrations of reactants and X is fractional extent of exchange at time t. Authors suggest mechanism involves direct reaction of thiol ion rather than catalysis by OH^-. Since $[OH^-] < B$ the $[OH^-] \simeq [n\text{-}C_4H_9S^-]$. **(.2)** Rate constant not calculated from R since $[OH^-] > B$ and authors do not give sufficient proof of rate law to validate such a calculation. Value of rate constant listed was extrapolated to 25° by authors and at best only gives order of magnitude.

LITERATURE

(1) A. Fava, A. Iliceto, E. Camera, *ACS* 1957, **79**, 833. (2) G.M. Harris, *TFS* 1951, **47**, 716.

ISOTOPIC EXCHANGE
Halogen on IVth group halides

Liquid phase
Amounts in M/l. Rate constants in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		$\Delta S^{\ddagger}$
						k^o	n		A^o	n	
.1	$SnCl_2 + Sn^*Cl_4 \longrightarrow Sn^*Cl_2 + SnCl_4$	C_2H_5OH	$10^2A=2-10$; $10^2B=2-20$	kAB	25	6.0	-5				
					29	1.04	-4				
					36	2.31	-4				
					42	5.3	-4	24	1	13	+16

COMMENTS

Reaction homogeneous as addition of glass wool and pyrex helices did not effect rate.

LITERATURE

E.G. Meyer, M. Kahn, *ACS* 1951, **73**, 4950.

ISOTOPE EXCHANGE

Halogen for halogen, in organic compounds

Liquid phase

Reaction types:

$$RX + X^{*-} \longrightarrow RX^{*} + X^{-}$$
(A) (B) (L) (M)

or $$RX + \tfrac{1}{2}X_2^{*} \longrightarrow RX^{*} + \tfrac{1}{2}X_2$$

Amounts are in M/l. Rate constants are in M/l and sec.

A = concentration of A + L and B = analytical concentration of B + M unless stated otherwise

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Saturated Alkyl Halide															
.19		$CH_3Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.3; B≃0.03	Li^+	= B	k AB	-3	1.09	-6					(2)
								25	3.88	-5					
								45	3.18	-4	20.1	2	10		
.20		$CH_3Br + Br^{*-}$	$(CH_3)_2CO$	A = 0.15-0.2; B = 0.024	Li^+	= B	k AB	-31	2.68	-4				*	(3)
								-25	6.30	-4					
								-18	1.46	-3					
								-11	3.40	-3	15.8	5	10		
.21		$C_2H_5Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.2; B≃0.03	Li^+	= B	k AB	25	5.5	-7					(2)
								40	3.09	-6					
								60	2.40	-5	21.5	3	9		
.22		$C_2H_5Br + Br^{*-}$	$(CH_3)_2CO$	A≃0.2; B=0.024	Li^+	= B	k AB	-11	2.89	-5				*	(3)
								0	1.06	-4					
								8	2.76	-4					

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.22		$C_2H_5Br + Br^{*-}$ *(continued)*	$(CH_3)_2CO$	A≃0.2; B=0.024	Li^+	= B	k AB	16	6.62	-4				*	(3)
								25	1.70	-3	17.5	1.3	10		
.23	.1	$C_2H_5I + I^{*-}$	CH_3OH	A = 0.04; 10^4B = 2-70	Na^+	= B		25	8.0	-5				*	(7) (8)
			C_2H_5OH	A=0.9; B=0.14			k AB	20	1.08	-4				*	(21)
				0.9-4 0.017				30	4.3	-4					
				0.030				30	4.4	-4					
				0.075				30	3.4	-4					
				0.15				30	3.3	-4					
				0.6				30	2.3	-4					
				1.5				30	2.2	-4					
				0.9 0.14				40	9.0	-4					
				0.14				50	3.2	-3	19				
				A=0.02; B=0.017				50	2.89	-3				*	(28)
								60	7.81	-3					
								70	2.07	-2	21.3	7	11		
			$(CH_3)_2CO$	A≃0.3; B=0.10				-27	1.23	-4				*	(4)
								-17	4.90	-4					
								- 6	2.18	-3	17.4	3	11		
.24		n-$C_3H_7Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.1; B≃0.03	Li^+	= B	k AB	44	4.21	-6				*	(37)
			$(CH_3)_2CO$ + 20% CH_3NO_2					44	1.73	-6					
.25		$(CH_3)_2CHCl + Cl^{*-}$	$(CH_3)_2CO$	A=0.2; B=0.028	Li^+	= B	k AB	60	4.55	-7					(2)
.26	.3	n-$C_3H_7Br + Br^{*-}$	H_2O	A = B = 0.1	Na^+	= B	k AB	35	2.13	-5					(22)
								61	2.13	-4					
								79	8.4	-4					
								100	3.6	-3	18				

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.26	.3	$n\text{-}C_3H_7Br + Br^{*-}$ *(continued)*	$(CH_3)_2CO$	A = 0.16; B = 0.024	Li^+	= B	k AB	-7	3.30	-5				*	(3)
								15	4.10	-4					
								25	1.08	-3					(5)
								31	1.91	-3	17.5	6	9		(3)
			CH_3NO_2	B = 0.024	$(C_2H_5)_4N^+$	= B	k AB	25	2.4	-4					(5)
.27	.4	$(CH_3)_2CHBr + Br^{*-}$	$(CH_3)_2CO$	A ≃ 0.2; B = 0.024	Li^+	= B	k AB	35	5.07	-5				*	(3)
				0.024				42	1.05	-4					
				0.024				50	2.46	-4					
				0.017				58	5.30	-4					
				0.024				58	4.67	-4					
				0.060				58	3.6	-4					
				0.024				65	9.74	-4	19.7	5	9		
			$(CH_3)_2CO$	A = 0.1; 10^3B = 5-50			$k'\alpha$ AB	20	4.86	-5				*	(15)
								40	4.43	-4					
				(α = degree of dissociation of LiBr)				60	2.95	-3	20.0	4	10		
.28	.7	$n\text{-}C_3H_7I + I^{*-}$	C_2H_5OH	A = 0.75; B = 0.14	Na^+	= B	k AB	35	3.7	-4				*	(21)
				" "				45	9.4	-4					
				0.02 0.017				50	1.95	-3				*	(28)
				0.75 0.14				55	2.35	-3	19				(21)
				0.02 0.017				60	5.33	-3					(28)
				" "				70	1.36	-2	20.8	2.5	11		
.29	.8	$(CH_3)_2CHI + I^{*-}$	C_2H_5OH	A = 0.02; B = 0.017	Na^+	= B	k AB	45	5.6	-5				*	(28)
								60	3.42	-4					
								70	9.6	-4	23.8	1.4	12		

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.29	.8	$(CH_3)_2CHI + I^{*-}$ *(continued)*	C_2H_5OH	A = 1.62; B = 0.14	Na^+	= B	k AB	45	6.4	-5				*	([21])
								55	1.04	-4					
								60	2.6	-4					
								70	7.0	-4	20.5	7	9		
			$(CH_3)_2CO$	A = 0.12; B = 0.1	Na^+	= B		0	2.93	-5				*	([4])
								25	5.87	-4	19.4	1	11		
.30		$C_2H_5(CH_3)CHCl + SnCl_4^*$	n-C_7H_{16}	A = 0.06-0.47; B = 0.008-0.065		k AB/(K + A)		160	3.8	-6				*	([13])
								200	~1	-4					
								160	K = 1.5	-1					
.31	.10	n-$C_4H_9Br + Br^{*-}$	$(CH_3)_2CO$	A = 0.04; 10^4B = 0.5	Li^+	= B	k AB	26	3.93	-3				*	([7]) ([8])
				2.5				26	3.13	-3					
				17.1				26	2.56	-3					
				79				26	1.44	-3					
				191				26	1.07	-3					
.32		$(CH_3)_2CHCH_2Br + Br^{*-}$	$(CH_3)_2CO$	A = 0.14-0.17; B = 0.024	Li^+	= B	k AB	25	5.82	-5				*	([3])
								33	1.40	-4					
								42	3.43	-4					
								50	7.04	-4					
								58	1.44	-3	18.9	4	9		
.33	.13	$(CH_3)_3CBr + Br^{*-}$	$(CH_3)_2CO$	A = 0.16; B = 0.024	Li^+	= B	k AB	25	5.26	-6				*	([3]) ([5])
								40	3.03	-5					([3])
								49	8.46	-5					
								60	2.58	-4					
								71	7.35	-4					
								79	1.46	-3	21.8	5	10		

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.33	.13	$(CH_3)_3CBr + Br^{*-}$ *(continued)*	$(CH_3)_2CO$	A = 0.07; B = 0.05	Li^+	= B	k AB	25	4.06	-6				*	(3)
								35	1.50	-5					
								44	3.99	-5					
								60	1.91	-4					
				A = 0.1;	Li^+	= B	k_1A +	20	$k_1$3.6	-8				*	(15)
				B = 0.005-0.1			$k_2\alpha$ AB	20	$k_2$5.5	-6					
								40	$k_1$3.2	-7					
				(α = degree of dissociation of LiBr)				40	$k_2$6.05	-5					
								60	$k_1$2.0	-6	19.7	1.6	7		
								60	$k_2$4.87	-4	21.8	1.0	11		
			CH_3NO_2	A = 0.05; B = 0.023	$(C_2H_5)_4N^+$	= B	k A	22	2.98	-6				*	(5)
				0.012				41	2.62	-5					
				0.024				41	2.53	-5					
				0.048				41	2.88	-5					
				0.022				50	6.54	-5	20.6	6	9		
.34		n-$C_4H_9I + I^{*-}$	C_2H_5OH	A = 0.6; B = 0.14	Na^+	= B	k AB	30	1.65	-4				*	(21)
								40	4.4	-4					
								50	1.09	-3					
								60	2.85	-3	19				
			CH_3CN	A = 0.05; B = 0.01	Li^+	= B	k AB	0	1.9	-4				*	(11)
				0.05 0.01				14	1.0	-3					
				0.05 0.01				29	4.8	-3					
				0.025 0.025				29	4.4	-3					
				0.024 0.01				48	3.0	-2	18.2				
				0.02-0.3 0.01	Na^+	= B	k AB	0	1.8	-4					
				0.05 0.01				14	1.1	-3					
				0.25 0.01				29	4.3	-3					
				0.25 0.05				29	4.1	-3					

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.34	n-$C_4H_9I + I^{*-}$ *(continued)*	CH_3CN	A = 0.01; B = 0.01	Na^+	= B	k AB	48	2.65	-2	18.0			*	([11])
			0.05 0.008	Cs^+	= B	k AB	0	2.1	-4					
			0.05 0.01				12	8.3	-4					
			0.05 0.005				29	5.8	-3					
			0.05 0.008				29	5.2	-3					
			0.005 0.005				40	2.0	-2	18.2				
			0.48 0.096	Zn^{++}	= ½B	k AB	48	1.7	-6					
			0.47 0.094				60	6.1	-6					
			0.46 0.092				81	3.92	-5					
			0.2-0.4 0.02-0.04				100	2.98	-4					
			0.04 0.09				122	1.25	-3	21.9				
			0.5 0.10	Cd^{++}	= ½B	k AB^2	30	2.16	-5					
			0.5 0.10				48	1.61	-4					
			0.24 0.09				60	5.23	-4					
			0.1-0.2 0.05				82	3.99	-3					
			0.2 0.09				82	3.61	-3	20.6				
.35	n-$C_4H_9I + HI^*$	$CH_3C_6H_5$				k AB	49	< 1	-7				*	([10])
		CH_3OH	A = 0.2-0.6; B = 0.075				0	2.42	-6					
			0.056				25	4.5	-5					
			0.041				36	1.46	-4					
			0.107				36	1.33	-4					
			0.075				49	4.14	-4	18.6	6	12		
		C_2H_5OH	A = 0.2-0.6; B = 0.054				0	5.97	-6					
			0.010				25	1.44	-4					
			0.034				25	1.30	-4					
			0.10				25	1.15	-4					
			0.34				25	9.25	-5					
			0.36				35	3.53	-4					
			0.36				45	1.55	-3	19.5	1.0	14		

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.35	n-C_4H_9I + HI* *(continued)*	C_4H_9OH	A = 0.1-0.6; B = 0.10			k AB	0	7.22	-6				*	([10])
			0.10				25	1.56	-4					
			0.039				36	5.20	-4					
			0.17				36	5.17	-4					
			0.039				49	1.71	-3	19.4	1.0	14		
		$C_6H_{13}OH$	A = 0.2-0.8; B = 0.10				0	7.67	-6					
			0.025				25	1.01	-4					
			0.10				25	1.34	-4					
			0.34				25	1.50	-4					
			0.68				25	1.53	-4					
			0.044				36	4.30	-4					
			0.12				36	4.58	-4					
			0.076				49	1.29	-3	18.4	2	13		
		$C_{12}H_{25}OH$	A = 1.0; B = 0.012				25	4.83	-5					
			0.060				25	6.90	-5					
			0.125				25	8.86	-5					
			0.251				25	9.70	-5					
			0.318				25	1.07	-4					
		CH_3COOH	A = 1.0; B = 0.082			k AB	0	1.19	-6					
			" 0.015				25	9.78	-6					
			" 0.052				25	1.45	-5					
			0.62 0.062				25	1.70	-5					
			1.0 0.21				25	2.81	-5					
			" 0.31				25	2.72	-5					
			" 0.082				36	5.55	-5					
			0.72 0.047				49	1.65	-4					
			0.29 0.12				49	2.02	-4	18.2	1.3	12		

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.36	$n\text{-}C_4H_9I + \frac{1}{2}I_2^*$	CH_3CN	A = 0.09; B = 0.02			k AB	70	5.70	-5					(11)
			0.09 0.02				81	1.25	-4					
			0.09 0.02				100	5.14	-4					
			0.04-0.09 0.02-0.04				122	1.94	-3	17.5				
.37	$(CH_3)_2CHCH_2I + I^{*-}$	C_2H_5OH	A = 1.4; B = 0.14	Na^+	= B	k AB	40	5.9	-5				*	(21)
							50	1.50	-4					
							60	3.5	-4					
							70	8.5	-4	19				
.38	$C_2H_5(CH_3)CHI + I^{*-}$	C_2H_5OH	A = 1.4; B = 0.14	Na^+	= B	k AB	45	7.0	-5				*	(21)
							50	1.22	-4					
							60	3.2	-4					
							70	8.8	-4	20.5				
.39	$(CH_3)_3CI + I^{*-}$	C_2H_5OH	A = 1.2; B = 0.37	Na^+	= B	k AB	40	9.4	-4					(21)
		$(CH_3)_2CO$	0.2 0.10	Na^+	= B		0	6.30	-6				*	(4)
			0.1-0.5 0.10				25	1.82	-4					
			0.1 0.10				45	1.58	-3	21.5	1.0	12		
.40	$(CH_3)_3CCH_2Br + Br^{*-}$	$(CH_3)_2CO$	A ≃ 0.2; B = 0.024	Li^+	= B	k AB	89	1.88	-5				*	(3)
							105	7.10	-5					
							116	1.61	-4					
							124	2.80	-4					
							135	5.89	-4	22.0	4	8		
.41	$n\text{-}C_5H_{11}I + I^{*-}$	C_2H_5OH	A = 0.6; B = 0.14	Na^+	= B	k AB	40	5.3	-4					(21)
							50	1.36	-3					
							60	3.56	-3	19				

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.42	$(CH_3)_2CHCH_2CH_2I + I^{*-}$	C_2H_5OH	A = 0.7; B = 0.14	Na^+	= B	k AB	50	5.7	-4					(21)
.43	$(CH_3)_3CCH_2I + I^{*-}$	$(CH_3)_2CO$	A ≃ 0.2; B = 0.10	Na^+	= B	k AB	35	4.48	-6				*	(4)
							45	1.13	-5					
							65	9.06	-5	22.0	1.6	10		
.44	$\overline{CH_2CH_2CH_2CH_2CH_2}CHCH_2Br + Br^{*-}$	$(CH_2OOCCH_3)_2$	A = 0.05; B = 0.030	Li^+	= B	k AB	90	1.23	-4				*	(34)
							100	2.67	-4					
							111	6.13	-4					
							122	1.19	-3	20.2	1.3	8		
.45	$C_5H_{11}(CH_3)CHI + I^{*-}$	C_2H_5OH				k AB	25	7.7	-6	21.8	8	10	*	(36)
.46	$C_6H_{13}(CH_3)CHBr + Br^{*-}$	$(CH_3)_2CO$	10^2A = 4-5; 10^4B = 2.61	Li^+	= B	k AB	66	7.21	-3				*	(7)
			3.02				66	7.05	-3					
			8.61				66	4.94	-3					
			15.7				66	4.15	-3					
			78.0				66	2.34	-3					
			150				66	1.53	-3					
			250				66	1.32	-3					
			700				66	8.3	-4					
			1400				66	7.7	-4					
			10^4B = 2-1400			$k'\alpha$ AB	66	1.10	-2	(α = degree of dissociation of LiBr)				
	Cyclo-Alkyl halides													
.47	*cyclo*-$C_5H_9I + I^{*-}$	C_2H_5OH	A = 0.2-0.5; B = 0.1-0.4			k AB	25	(8.8)	-6				*	(36)
							37	3.2	-5					

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.47	*cyclo*-$C_5H_9I + I^{*-}$ *(continued)*	C_2H_5OH	A = 0.2-0.5; B = 0.1-0.4			*k* AB	47	9.0	-5				*	(36)
							56	2.49	-4					
							64	4.79	-4	21.0	2	10		
.48	*cyclo*-$C_6H_{11}I + I^{*-}$	C_2H_5OH	A = B = 0.30			*k* AB	69	2.3	-7					(36)
							80	6.2	-7					
							90	2.12	-6					
							100	5.12	-6	25.6	5	11		
.49	*cyclo*-$C_7H_{13}I + I^{*-}$	C_2H_5OH				*k* AB	25	(1.2)	-5	21.3	5	10	*	(36)
.50	*cyclo*-$C_8H_{15}I + I^{*-}$	C_2H_5OH				*k* AB	25	(2.8)	-6	22.0	4	10	*	(36)
.51	*bicyclo*-$C_{10}H_{17}Cl + HCl^*$ (camphene hydrochloride)	$CHCl_3$	A = 0.16; B = 0.1-0.16			*k* AB	0	1.5	-3				*	(23)
.52	*bicyclo*-$C_{10}H_{17}Cl + DCl^*$ (camphene hydrochloride)	$CHCl_3$	A = 0.16; B = 0.02-0.1			*k* AB	0	1.4	-3				*	(23)
.53	*cyclo*-$C_{15}H_{29}I + I^{*-}$	C_2H_5OH				*k* AB	25	(9.9)	-7	20.1	6	8	*	(36)
	Carboxyl-substituted alkyl halides													
.54	$CH_2ICOOH + I^{*-}$	H_2O	10^3A = 3-9; 10^3B = 3-20	H_2SO_4	0.005-0.01	*k* AB	25	8.7	-3					(33)
							60	1.49	-1	16	5	9		
.55	$CH_2ICOOH + I_2^*$	H_2O				*k* AB	25	5	-4					(33)
.56	$CH_2ICOOH + I_3^{*-}$	H_2O	10^3A = 9; 10^3B = 1.5-3	I^-	0.0046-B	*k* AB	25	<< 8	-3					(33)

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.57	$CH_2ICOO^- + I^{*-}$	H_2O	$10^3A = 3-7$; $10^3B = 8-17$	NaOH	0.01-0.02	k AB	25	8.0	-4					(33)
							60	1.49	-2	16	5	8		
.58	$CH_2ICOOCH_3 + I^{*-}$	H_2O	$10^3A = 4-7$; $10^3B = 7-15$			k AB	0	5.8	-4					(33)
							25	7.5	-3	17	2	10		
	Halogen-substituted alkyl halide													
.59	$CH_2I_2 + I^{*-}$	C_2H_5OH	A = 0.5; B = 0.06	Na^+	= B	k AB	60	1.04	-3					(21)
.60	$CCl_3Br + BrBr^*$	A	B = 0.03-0.08			k $AB^{\frac{1}{2}}$	100	1.0	-6				*	(38)
							115	5.1	-6					
							125	1.33	-5					
							135	3.3	-5	30				
		CCl_4	A = 0.2-0.9; $10^3B = 3-8$				135	2.8	-5					
							150	7.5	-5					
							170	5.5	-4	29				
	Unsaturated alkenyl halide													
.61	$CH_2{:}CHCH_2Cl + Cl^{*-}$	$(CH_3)_2CO$	$A \simeq 0.1$; $B \simeq 0.03$	Li^+	= B	k AB	44	5.87	-5				*	(37)
		$(CH_3)_2CO$ + 20% CH_3NO_2		Li^+	= B		44	4.21	-5					
.62	$CH_2{:}CHCH_2I + I^{*-}$	C_2H_5OH	A = B = 0.01	Na^+	= B	k A	14	5.0	-5				*	(16)
							22	1.07	-4					
							28	2.2	-4					
							41	7.1	-4	17				

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.63	$CH_2{:}CHCH_2I + I_2^*$	C_6H_{14}	10^3A = 7-300; 10^5B = 6-400	(dark)		k AB	0	7.7	-4				*	(24) (29)
							15	2.37	-3					
							25	6.0	-3					
							35	1.15	-2					
							40	1.74	-2	13.1	2.5	7		
.64	$CH_2{:}CHCH_2I + I^*$	C_6H_{14}	10^3A = 3-100			k AB	25	5	+6				*	(30)
.65	$CH_3CH{:}CHCH_2Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.1; B≃0.03	Li^+	= B	k AB	44	1.48	-4				*	(37)
.66	$CH_2{:}CH(CH_3)CHCl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.1; B≃0.03	Li^+	= B	k AB	44	1.82	-6				*	(37)
.67	$CH_3CH{:}CHCH_2Br + Br^{*-}$	$(CH_3)_2CO$	A=0.1; B=0.04	Li^+	= B	k AB	-33	3.49	-4				*	(6)
							-27	7.13	-4					
							-19	1.98	-3	14.7	2	9		
.68	$CH_2{:}CH(CH_3)CHBr + Br^{*-}$	$(CH_3)_2CO$	A=0.1; B=0.04	Li^+	= B	k AB	- 6	3.44	-5				*	(6)
							16	3.67	-4					
							25	8.66	-4					
							30	1.42	-3	16.5	1.1	9		
.69	$(CH_3)_2C{:}CHCH_2Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.1; B≃0.03	Li^+	= B	k AB	44	1.25	-3				*	(37)
Unsaturated alkynyl halides														
.70	$CH{:}CCH_2Cl + Cl^{*-}$	$(CH_3)_2CO$	A≃0.1; B≃0.03	Li^+	= B	k AB	44	6.57	-5				*	(37)
Unsaturated alkenyl Di-halides														
.71	*cis*-or-*trans*-$BrCH{:}CHBr + Br_2^*$	CCl_4	A=0.17; B=0.01			k $AB^{\frac{1}{2}}$	30	7.5	-6				*	(31)

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.71		*cis*-or-*trans*-BrCH:CHBr + Br_2* *(continued)*	CCl_4	A = 0.17; B = 0.01			$k\,AB^{\frac{1}{2}}$	36	1.50	-5				*	(31)
								45	4.4	-5	22	1	11		
.72		*cis*-ICH:CHI + I_2*	decalin	10^3A = 5-30; 10^3B = 3-13	decalin		$k\,AB^{\frac{1}{2}}$	76	1.2	-5				*	(24a)
								100	1.25	-4	25	4	9		
.73	.2	*trans*-ICH:CHI + I_2*	decalin	10^3A = 5-30; 10^3B = 3-13			$k\,AB^{\frac{1}{2}}$	100	1.0	-4	26	6	9	*	(24a)
			C_6H_{14}	A = 0.1; 10^5B = 3.5				25	8.3	-9				*	(40)
				10^4B = 3.3				25	1.6	-8					
				10^5B = 3.5	H_2O	trace		25	4	-8					
.74		*trans*-ICH:CHI + I*	C_6H_{14}	A = 0.02-0.2; $10^5[I_2]$ = 3.5			$k\,AB$	25	2.6	+3	8	4	9	*	(26)
Aryl-substituted alkyl halide															
.75		$C_6H_5CH_2Br$ + Br^{*-}	$(CH_3COOCH_2)_2$	A = 0.05; B = 0.03	Li^+	= B	$k\,AB$	6	1.21	-4					(34)
								17	3.38	-4					
								25	7.89	-4					
								35	1.68	-3					
								45	3.64	-3	15.3	7	7		
.76		$C_6H_5CH_2I$ + I^{*-}	CH_3OH	10^3A = 1-10; 10^3B = 1-10	K^+	= B	$k\,AB$	0	1.0	-3				*	(32)
								27	1.5	-2					
								44	6.4	-2	16.2	1.0	10		
			C_2H_5OH	10^3A = 1-14; 10^4B = 8-130	K^+	= B		0	1.65	-4					
								27	2.87	-3					
								44	1.40	-2	17.3	1.2	11		

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.77	$C_6H_5CH_2I + I_2^*$	$CCl_2{:}CClCCl{:}CCl_2$	10^4A = 1-1500; 10^5B = 3-5000			$k\,AB^{\frac{1}{2}}$	60	2.15	-5				*	(9)
							70	6.20	-5					
							80	2.00	-4					
							90	5.41	-4	26.1	3	12		
.78	p-$CH_3OC_6H_4CH_2Br + Br^{*-}$	$(CH_3COOCH_2)_2$	A = 0.05; B = 0.03	Li^+	= B	$k\,AB$	-5	3.14	-4				*	(34)
							5	8.33	-4					
							15	2.00	-3					
							25	4.52	-3	13.9	5	7		
.79	p-$N{:}CC_6H_4CH_2Br + Br^{*-}$	$(CH_3COOCH_2)_2$	A = 0.05; B = 0.03	Li^+	= B	$k\,AB$	-7	2.29	-4				*	(34)
							5	9.47	-4					
							15	2.71	-3					
							25	7.59	-3	16.8	1.0	10		
.80	p-$NO_2C_6H_4CH_2Br + Br^{*-}$	AnM^*	A = 0.05; 10^4B = 1.2	Li^+	= B	$k\,AB$	0	8.98	-3				*	(1)
			6.0				0	8.16	-3					
			21				0	5.62	-3					
			104				0	4.33	-3					
			380				0	1.98	-3					
			1.2				30	2.23	-1					
			4.9				30	1.60	-1					
			12				30	1.34	-1					
			102				30	9.57	-2					
			313				30	7.5	-2					
						$k_1 = k/\alpha$	0	1.01	-2					
			(α = calculated degree of dissociation of LiBr)				30	2.21	-1	16	1	11		
		$(CH_3COOCH_2)_2$	10^2A = 2-10; 10^2B = 1-10	Li^+	= B	$k\,AB$	-5	4.57	-4				*	(34)
							0	7.56	-4					
							11	2.45	-3					
							20	5.41	-3	15.4	1.0	9		

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.81	$p\text{-}NO_2C_6H_4CH_2I + I^{*-}$	CH_3OH	$10^4A = 5\text{-}30$; $10^4B = 4\text{-}30$	K^+	= B	$k\,AB$	0	2.2	-3				*	(27)
							20	1.5	-2					
							31	4.0	-2	15.6	6	9		
		C_2H_5OH					0	6.0	-3					
							20	5.0	-2					
							31	1.32	-1	16.5	9	10		
.82	$2,4\text{-}(NO_2)_2C_6H_4CH_2Br + Br^{*-}$	$(CH_3COOCH_2)_2$	A = 0.05; B = 0.03	Li^+	= B	$k\,AB$	-27	3.10	-4				*	(34)
							-20	8.16	-4					
							- 7	4.20	-3	16.4	1.2	11		
.83	$(C_6H_5)_3CCl + (C_{18}H_{38})_2(CH_3)_2NCl^*$	C_6H_6	A = 0.03; $10^4B = 6\text{-}70$			$k\,A$	36	3.3	-5					(35)
							50	7.9	-5					
				$(C_{18}H_{38})_2(CH_3)_2NF$	0.017		50	1.3	-5	$\Delta H^\ddagger$	$\Delta S^\ddagger$			
					0		68	2.34	-4	12.4	-39			
			$10^3B > 7$			$k\,A + k'\,AB^{3.7}$	50	$k' = 9.9$	+3					
			$10^3B < 7$	C_6H_5OH (X)		$\gtrless B\,k\,A + k''AX$	50	$k'' = 1.05$	-1					
	Aryl halides													
.84	$C_6H_5I + I^{*-}$	$CH_3C{:}N$	A = 0.74; B = 0.041			$k\,A$	157	5.0	-10				*	(14)
			0.74 0.082				157	1.0	-9					
			0.33 0.164				157	2.8	-9					
			0.72 0.039				185	6.1	-9					
			0.72 0.079				185	5.6	-9					
			0.32 0.158				185	6.9	-9					
			0.69 0.038				207	2.2	-8					
			0.69 0.076				207	3.1	-8					
			0.31 0.153				207	2.4	-8					

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.84	$C_6H_5I + I^{*-}$ *(continued)*	$CH_3C{:}N$	A = 0.66; B = 0.037			k A	238	2.5	-7				*	([14])
			0.66 0.074				238	3.0	-7					
			0.29 0.147				238	1.4	-7	24				
		2-$C_8H_{17}OH$	A = 0.02; B = 0.010	Na^+	= B	k A	240	1.9	-8				*	([20])
			0.020				240	1.7	-8					
			0.040				240	1.4	-8					
			0.10				240	1.6	-8					
.85	p-$HOC_6H_4I + I^{*-}$	2-$C_8H_{17}OH$	A = 0.02; B = 0.018	Na^+	= B	k A	192	4.6	-6				*	([18])
			0.01-0.02 0.01-0.1				200	7.5	-6					
			0.02 0.018				215	1.5	-5					
			0.02 0.02				231	4.2	-5					
			0.04				231	3.6	-5					
			0.1				231	3.4	-5					
.86	o-$NO_2C_6H_4I + I^{*-}$	$CH_3C{:}N$	A = 0.18; B = 0.04			k AB	100	1.3	-6				*	([14])
			0.18 0.09				100	7.2	-7					
			0.04 0.18				100	1	-7					
			0.04 0.16				157	6.4	-6					
			0.08 0.33				157	5.0	-6					
			0.16 0.04				157	2.0	-5					
			0.16 0.08				157	1.2	-5					
			0.33 0.08				157	3.4	-5					
			0.04 0.16				185	3.8	-5					
			0.16 0.04				185	8.3	-5					
			0.16 0.08				185	7.1	-5					
			0.04 0.08				207	1.96	-4					
			0.04 0.15				207	1.8	-4					
			0.08-0.15 0.04-0.08				207	2.5	-4					

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.86	$o\text{-}NO_2C_6H_4I + I^{*-}$ *(continued)*	$CH_3C{:}N$	A = 0.04; B = 0.15			k AB	238	8.9	-4				*	(14)
			0.15 0.04				238	1.66	-3	29				
.87	$m\text{-}NO_2C_6H_4I + I^{*-}$	$CH_3C{:}N$	A = 0.2-0.4; B = 0.04-0.16			k A	157	8	-9				*	(14)
							185	3.6	-8					
							207	1.3	-7					
							238	9.4	-7	25				
.88	$p\text{-}NO_2C_6H_4I + I^{*-}$	$CH_3C{:}N$	A = 0.04; B = 0.09			k AB	100	8	-9				*	(14)
			0.09 0.04				100	4.4	-7					
			0.04 0.08				157	1.4	-6					
			0.08 0.04				157	2.1	-6					
			0.04 0.08				185	9.7	-6					
			0.08 0.04				185	1.3	-5					
			0.04 0.08				207	4.81	-5					
			0.08 0.04				207	5.7	-5					
			0.2 0.04				202	5.0	-5					
			0.04 0.08				238	3.6	-4					
			0.07 0.04				238	5.0	-4	34				
			0.01-0.02 0.02				240	4.8	-4				*	(19)
			0.02 0.06-0.12				240	3.8	-4					
		$2\text{-}C_8H_{17}OH$				k A	240	1.46	-4					
.89	$2,4,6\text{-}(NO_2)_3C_6H_2Br + Br^{*-}$	$(CH_3COOCH_2)_2$	A = 0.05; B = 0.030			k AB	-5	1.99	-4				*	(34)
							0	3.92	-4					
							10	1.31	-3					
							22	4.53	-3	18.2	9	10		
.90	$HOOCCH(NH_2)CH_2\text{-}4\text{-}HOC_6H_2\text{-}3,5\text{-}I_2 + I^{*-}$	H_2O					63	(no exchange in 2 weeks)						(39)

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.91	$HOOCCH(NH_2)CH_2$-4-HOC_6H_2-3,5-I_2 + II^*	H_2O	10^5A = 4-1500; 10^5B = 1-40	CH_3COOH	pH	$k\,AB[H^+]^{-1}$	20	5.33	-4				*	([39])
				CH_3COONa	3.5-5.2		31	2.07	-3					
				H_2SO_4			42	8.11	-3	23	8	13		
				$NaHSO_4$	1.3-2.5									

SOLVENTS

AnM* $(CH_3)_2CO$ + 5 vol % CH_3OH

COMMENTS

General. The halogens marked X^* are radioactive isotopes. Pseudo first order exchange rates are observed, and isotope effect, (appreciable difference between rate constants for forward and reverse reaction) is considered negligible. The kinetic rate law and the chemical reaction rate constant are calculated from the dependence of the exchange rate, $R = \frac{-2.303ab}{(a+b)\,t}\log(1-x/x_\infty)$, upon the concentrations of A+L and B+M and any catalysts, where a is the stationary concentration A+L, b is the stationary concentration B+M, and x/x_∞ is the measured ratio (at time t) of the concentration of the labeled isotope in the molecular species in which it was not introduced to its concentration at infinite time in that same species. The exchange rate R = f(a, b, catalyst) such as $k\,AB$, $k\,AB^{\frac{1}{2}}$ or more complex expressions. For a more complete treatment see ([9a])([21a]). Rates of exchanges involving halogen salts in nonaqueous media in general parallel apparent degree of ionization from conductivity data. For this reason the reacting species is listed as the halogen ion, but the rate constants and concentrations are in terms of the total analytical, ionized and unionized salt concentration.

Reaction. (.20) (.22) Values of rate constants at concen-

COMMENTS *(continued)*

tration, (b), other than 0.024 M/l converted to this concentration by the empirical relation

$$\log(k_b/k_{0.024}) = -0.37 \log(b/0.024).$$

([3]) found this transformation valid for each alkyl bromide studied over a temperature range from 26° to 65°C and for $10^3 b$ = 1.6 to 100. **(.23)** Values of rate constants by ([28]) corrected from erroneous values in 1951 Edition of Tables. Selected values listed from ([7])([8]). Negative salt effect observed by ([4]) who converted values of rate constants to the same concentration NaI by empirical equation, see (.20)(.22). **(.24)** Converted to sec. from original min. **(.26)** Negative salt effect observed by ([3]) who converted values of rate constants to the same concentration of LiBr by empirical equation, see (.20)(.22). **(.27)** Negative salt effect. Rate constants converted by ([3]) to the same concentration of LiBr by empirical equation, see (.20)(.22). ([15]) obtained straight line in plot of exchange rate divided by (A+L), R/(A+L), versus α(B+M) where α is the degree of dissociation of LiBr from conductivity measurements. Negligible intercept may be taken to indicate the low reactivity of undissociated salt. **(.28)** Values of rate constants by ([28]) corrected from erroneous values in 1951 Edition of Tables. **(.29)** Values of rate constants by ([28]) corrected from erroneous values in 1951 Edition of Tables. Negative salt effect. Selected data of ([21]). ([4]) converted rate constants to same concentrations of NaI by empirical equation, see (.20)(.22). **(.30)** Authors showed observed rate law to be consistent with mechanism involving fairly stable complex between reactants with K as the equilibrium constant for the dissociation of this complex. **(.31)** Selected data. **(.32)** Negative salt effect. Values of rate constants converted to the same concentration of LiBr by empirical equation, see (.20)(.22). **(.33)** Negative salt effect in acetone with LiBr. ([3]) converted values of rate constants to same concentration of LiBr by empirical equation, see (.20)(.22). ([15]) obtained straight line in plot of exchange rate divided by (A+L), R/(A+L), versus α(B+M) where α is the degree of dissociation of LiBr from conductivity measurements. The intercept and slope gave k_1 and k_2 respectively. A small positive salt effect observed by ([5]) in CH_3NO_2 with $(C_2H_5)_4NBr$ the halide salt. **(.34)** Selected data of ([11]) and ([21]). ([11]) proposed results to indicate that I^- is the reacting species for the alkali halides, the undissociated molecule or a complex ion in the

Supplement 1955

COMMENTS *(continued)*

case of ZnI_2 and an associated complex such as $CdCdI_4$ in the case of CdI_2 which showed third order behavior on the basis of a single variation in concentration of CdI_2 by a factor of only two. Units of ([11]) converted to sec. from original hours. **(.35)** Reacting species in all solvents studied considered to be I^- and not HI, however in *n*-hexanol, *n*-dodecanol and acetic acid authors consider simultaneous reactions involving I^- and HI_2^- contribute to rate. By estimating degree of dissociation of HI and of formation of HI_2^- from conductivity data values of the reaction rate constants for each reacting species were estimated. Units converted to sec. from original hrs. **(.37) (.38)** Selected data. **(.39)** Negative salt effect. ([4]) converted rate constants to same concentration of NaI by empirical equation, see (.20) (.22). Corrected for parallel reaction believed to be elimination with olefin formation. **(.40) (.43)** Negative salt effect. Rate constants were converted to same concentration of alkali halide by empirical equation, see (.20) (.22). **(.44)** E converted from original E' of ([34]) by adding ½RT. **(.45)** Rate constant at 25° extrapolated from measured values probably between 30° and 70°C. **(.46)** Selected data. **(.47) (.49) (.50)** Rate constants at 25°C extrapolated from measured values probably between 30° and 70°C. **(.51) (.52)** Rate of deuterium exchange between DCl and camphene hydrochloride about 20% faster than halogen exchange, see 302.401. **(.53)** Rate constant at 25°C extrapolated from measured values probably between 30° and 70°C. **(.60)** Units converted to sec. from original hrs. **(.61)** Units converted to sec. from original min. **(.62)** Units not stated and calculations not illustrated, assumed base e logarithms and sec. from calculations from illustrative curve. **(.63)** One hundred fifty fold variation in B+M shows only first order rate with respect to I_2 thus indicating molecular I_2 rather than atoms to be the reacting species. Addition of small amount of water caused no effect. Slight inhibition by O_2 from air as 12% increase in rate observed on sweeping N_2. **(.64)** Units converted to M/l from M/ml. I atoms produced photochemically and accuracy limited by estimation of concentration of atoms. **(.65) (.66)** Units converted to sec. from original min. **(.67) (.68)** Negative salt effect. Values converted to same concentration of LiBr. **(.69) (.70)** Units converted to sec. from original min. **(.71)** No difference observed in exchange rate for *cis*- and *trans*-isomers. Units converted

COMMENTS *(continued)*

to M/l from M/ml. **(.72)** Values corrected from erroneous values in 1951 Edition of Tables. Units converted to M/l from original M/ml. **(.73)** Units converted to sec. from hrs. **(.74)** Iodine atoms produced photochemically and accuracy dependent upon the determination of the concentration of atoms. Units converted to M/l from original M/ml. **(.76)** Units converted to sec. from original min. **(.77)** Reaction inhibited by oxygen. Considered to involve chain mechanism and rate constants for the seven individual steps calculated by authors. **(.78) (.79)** E converted from E' of authors by adding ½RT. **(.80)** In ethylene glycol diacetate E converted from E' of ([34]) by adding ½RT. **(.81)** Units converted to sec. from original min. **(.82)** E converted from E' of ([34]) by adding ½RT. **(.84)** First order constants erratic but show better agreement than calculated second order constants. Units converted to sec. from original hrs. Units and calculations not shown by ([20]) but assumed to be hrs. from comparison with values by ([14]). ([14]) observed formation of black precipitate at higher temperatures. Addition of free I_2 accelerated rate 10 to 15%. Addition of 0.5 gms. H_2O or Na_2SO_3 retarded rate about 15%. Selected data. **(.85)** No calculations shown, or units which were assumed to be hrs. and converted to sec. **(.86)** Free I_2 formed after about 30% exchange. I_2 made no noticeable effect on exchange rate. Units converted to sec. from original hrs. **(.87)** Units converted to sec. from original hrs. First order rate constants erratic but show less deviation than calculated second order constants. Appreciable free I_2 and black precipitate formed at 238°C. **(.88)** Units of ([14]) converted to sec. from original hrs. Units of ([19]) converted to M/l from original mM/l. First order rate constants showed less variation than calculated second order constants in 2-octanol. Second order rate constants showed less variation than calculated first order constants in acetonitrile. Method of calculation not indicated by ([19]). **(.89)** E converted from E' of ([34]) by adding ½RT. **(.91)** No exchange observed in 24 hr. period at 52°C with CH_3OH or C_2H_5OH as solvent.

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ISOTOPE EXCHANGE

Hydrogen Isotope between Vth Group Element and Oxygen

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$NH_4NO_3 + DNO_3 \longrightarrow NH_3DNO_3 + HNO_3$	H_2O	B = 11.6				0	60-600				(1)
.2	$NH_4NO_3 + TNO_3 \longrightarrow NH_3TNO_3 + HNO_3$	H_2O	B = 11.6				0	180				(2)
.3	$NH_4^+ + CH_3OD \longrightarrow NH_3D^+ + CH_3OH$	$HC{:}ON(CH_3)_2$	A = 0.3-0.5; B = 0.1	HBr	0.001-0.1	$k\,AB[H^+]^{-1}$	0		2.5	-5	*	(3)
		B	A = 0.1	HCl	0.06			rel. rate 1				
.4	$C_2H_5NH_3^+ + CH_3OD \longrightarrow C_2H_5NH_2D^+ + CH_3OH$	B	A = 0.1	HCl	0.06		0		0.07		*	(3)
.5	$(C_2H_5)_2NH_2^+ + CH_3OD \longrightarrow (C_2H_5)_2NHD^+ + CH_3OH$	B	A = 0.1	HCl	0.06		0		0.10		*	(3)
.6	$(CH_3)_3NH^+ + CH_3OD \longrightarrow (CH_3)_3ND^+ + CH_3OH$	B	A = 0.1	HCl	0.06		0		0.5		*	(3)
.7	$(CH_3)_3NH^+ + C_4H_9OT \longrightarrow (CH_3)_3NT^+ + C_4H_9OH$	$CHCl_3$	A = B = 0.1	Cl^-			0	120				(2)
.8	$(C_2H_5)_3NH^+ + CH_3OD \longrightarrow (C_2H_5)_3ND^+ + CH_3OH$	B	A = 0.1	HCl	0.06		0		9		*	(3)
.9	$(C_2H_5)_3NH^+ + C_4H_9OT \longrightarrow (C_2H_5)_3NT^+ + C_4H_9OH$	$CHCl_3$	A = B = 0.1	Cl^-			0	3.6×10^4				(2)
.10	$C_6H_5NH_3^+ + CH_3OD \longrightarrow C_6H_5NH_2D^+ + CH_3OH$	B	A = 0.1	HCl	0.06		0		> 100		*	(3)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.11	$PH_3 + HOD \longrightarrow PH_2D + H_2O$	B	A = sat. at 100-500 mm.	X = H_3O^+	+ buffering salt	k AX	27		3.6	0	*	([4])
				HCOOH		k AX	27		2.1	-3		
				CH_3COOH		k AX	27		9.4	-4		
				$(CH_3)_3CCOOH$		k AX	27		4.7	-4		
				OH^-		k AX	27		4.0	-1		

COMMENTS

Reactions: **(.3)** Rate constant calculated using rate law given by authors and half-time for exchange given at only one point. Exchange rate independent of which compound was labeled. This reaction used as reference for relative rates of alkyl substituted ammonium ions in methanol. No actual rates given. **(.4) (.5) (.6)** Relative rate with reference to (.3) as unity. **(.8)** Relative rate with reference to (.3) as unity. Negative salt effect observed with 30 % decrease in rate constant in methanol on going from 0.05 to 0.4 M/l initial concentration of A. Increasing polarity of solvent observed to usually decrease rate of exchange. Reaction immeasurably fast in toluene with rates in C_2H_5OH faster than in CH_3OH and slow in ethylene glycol. In organic acids as solvents, HCOOH or CH_3COOH, rate of exchange immeasurably fast. **(.10)** Rate relative to (.3) as unity. **(.11)** Reaction carried out in two phase system, gas and liquid, and rate constants corrected for amount of A in gas phase as exchange is limited to liquid phase. Conditions such that diffusion between phases was at least ten times faster than the reaction studied. General acid and base catalysis observed and rate of exchange is $\Sigma k_i A[\text{catalyst}]_i$. Catalyst constants for the acids were corrected for oxonium ion catalysis but no correction made for catalysis by conjugate base in buffer solution, (acid and conjugate base always equal.) Slight positive salt effect observed with NaCl at constant pH using benzoic acid, sodium benzoate buffer. Over temperature range 27-50°C activation energy for both H_3O^+ and OH^- catalysis is 17.6 Kcals. Preexponential term being 2.4×10^{13} and 2.7×10^{12} respectively.

LITERATURE

(1) A. I. Brodskii, L. V. Sulima, *Doklady Akad. Nauk. SSSR*, 1950, **74**, 513. (2) L. Kaplan, K. E. Wilzbach, *ACS* 1954, **76**, 2593. (3) C. G. Swain, J. T. McKnight, M. M. Labes, V. P. Kreiter, *ACS* 1954, **76**, 4243. (4) R. E. Weston, J. Bigeleisen, *ACS* 1954, **76**, 3074; R. E. Weston, J. Bigeleisen, *J.C.P.* 1952, **20**, 1400.

ISOTOPIC EXCHANGE

H - D exchange on N in VIIIth Group Complex

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments
.1	$Co(ND_3)_6^{+++} + 18H_2O \longrightarrow Co(NH_3)_6^{+++} + 18HOD$	B	10^3A = 6-60 10^2A = 4.8	Na_2HPO_4, KH_2PO_4	4.7-5.6 4.81	$k\,A[H^+]^{-1} = -dA/dt$	20 0 8 15 22	4.14 1.18 5.55 1.95 6.06	-9 -10 -10 -9 -9	28.4	*
.2	$Co(ND_2CH_2CH_2ND_2)_3^{+++} + 12H_2O \longrightarrow Co(NH_2CH_2CH_2NH_2)_3^{+++} + 12HOD$	B	10^2A = 3-14	Na_2HPO_4, KH_2PO_4	4.4-4.8	$k\,A[H^+]^{-1} = -dA/dt$	0 8 15 22	2.46 9.7 3.38 1.05	-10 -10 -9 -8	28.1	*

COMMENTS

Reaction. (.1) Pseudo first order exchange rate constant independent of concentration of A or fraction of heavy isotope in A. Observed pseudo first order constant inversely proportional to corrected hydrogen ion activity. pH of buffer dependent upon concentration of trivalent cobaltic ion. If this correction is not made exchange rate appears to be dependent upon $A^{-0.54}$ power. Addition of KCl or NH_4NO_3 had no effect on rate constant. (.2) Rate constant calculated by multiplying observed pseudo first order exchange rate constant by corrected hydrogen ion activity. Observed pH of buffer corrected for influence of triply charged cobaltic ion.

LITERATURE

J. S. Anderson, H. V. A. Briscoe, N. L. Spoor, *CSL* **1943**, 361.

ISOTOPIC EXCHANGE

H - D exchange on nitrogen

Liquid phase

Amounts are in M/l except where otherwise indicated.

Rate constants are in M/l and sec.

No.	Reaction	Method	Medium (Solvent)	Amount of reactants	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
.1	$D_2 + NH_2^- \longrightarrow HD + NHD^-$	mass sp.	NH_3	A = (sat. at 50-60 mm of Hg); 10^3B = 1.5-2.7	k AB	-50	8.2	+1	*
.2	$HD + NH_2^- \longrightarrow H_2 + NHD^-$	mass sp.	NH_3	A = (sat. at 0-30 mm of Hg); 10^3B = 1.5-2.7	k AB	-50	4.7	+1	*
.3	$ArD + NH_2^- \longrightarrow ArH + NHD^-$	infra red	NH_3	(See 302.402)					

COMMENTS

Reaction. **(.1)** Pseudo first order rate as B undergoes rapid exchange with solvent. Reaction followed by (.2). Considered to follow same mechanism as para-hydrogen conversion catalyzed by NH_2^-, see 102.000. **(.2)** Determined from integrated form of differential rate equation involving two consecutive first order reactions.

LITERATURE

W.K. Wilmarth, J.C. Dayton, *ACS* 1953, **75**, 4553.

EXCHANGE

Halogen replaced by H on aliphatic C

Gas phase

Reaction type: $RX + HX \longrightarrow RH + X_2$
(A) (B) (L) (M)

Rate measured: dM/dt

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
					k_1							
.1	$CH_3I + HI \longrightarrow CH_4 + I_2$	10^3A = 2-8; $10^3B \sim 3$	$k_1AB + k_2AB/B_o$	270	8.0	-3					*	(2)
				280	1.5	-2						
				290	2.5	-2						
				300	4.4	-2						
				310	7.2	-2						
				320	1.14	-1		33.4	2.3	11		
					k_2							
				270	2.7	-5						
				280	5.2	-5						
				290	1.03	-4						
				300	2.00	-4						
				310	3.58	-4						
				320	7.0	-4		43.0	3.9	12		
		10^3A = 2.3; 10^3B = 1.3		320	5.2	-4						
		0.4 0.8		320	5.7	-4						
		0.9 0.4		320	3.6	-4						
		0.3 0.2		320	2.4	-4						

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k_o	n	K	E	$A = A^o \times 10^n$ A_o	n	Comments	Literature
					k_1							
.2	$C_2H_5I + HI \longrightarrow C_2H_6 + I_2$	$10^3A = 1.1\text{-}2.5$; $10^3B = 4.2\text{-}5.0$	$k_1AB + k_2AB/B_o$	250	2.18	-2					*	(2)
				260	3.70	-2						
				280	1.02	-1						
				290	1.65	-1						
				300	2.63	-1		29.8	6.3	10		
					k_2							
				250	2.50	-5						
				260	5.5	-5						
				280	2.34	-4						
				290	4.7	-4						
				300	9.2	-4		43.0	1.8	13		
		$10^3A = 0.45$; $10^3B = 1.1$		300	9.1	-4						
		1.0 0.45		300	7.7	-4						
		0.12 0.34		300	6.6	-4						
		0.11 0.25		300	6.1	-4						
		0.13 0.20		300	5.7	-4						
		0.22 0.14		300	5.6	-4						
		0.13 0.17		300	4.5	-4						
					k_1							
.3	$n\text{-}C_3H_7I + HI \longrightarrow C_3H_8 + I_2$	$10^3A \sim 1$; $10^3B \sim 5$	$k_1AB + k_2AB/B_o$	260	1.67	-2					*	(2)
				270	2.84	-2						
				280	4.7	-2						
				290	7.6	-2						
				300	1.14	-1		29.2	1.6	10		
					k_2							
				260	8.3	-5						
				270	1.83	-4						
				280	3.7	-4						
				290	7.5	-4						
				300	1.40	-3		43.0	2.8	13		

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$Cl_3CBr + HBr \longrightarrow Cl_3CH + Br_2$	10^2A = 1.1-2.5; 10^3B = 0.5-39; 10^2M = 1.7-4.1	$k\,AM^{\frac{1}{2}}/(1 + KM/B)$	147	3.64	-5	24.5				*	(3)
				169	2.55	-4	24.8					
				182	7.57	-4	25.5	32.9	5	12		
.4.1	$Cl_3CBr + Br \longrightarrow Cl_3C^{\cdot} + Br_2$	10^2A = 1.1-2.5; 10^2M = 1.7-4.1	$k\,AB$	147-182				10.2	8.1	10	*	(3)
.4.2	$Cl_3C^{\cdot} + \begin{cases} HBr \longrightarrow Cl_3CH + Br & (1) \\ Br_2 \longrightarrow Cl_3CBr + Br & (2) \end{cases}$		k_1AB_1	~120	k_1/k_2 = 1.4	1					*	(1)
			k_2AB_2	147	4.1	0						(3)
				169	4.0	0						
				182	3.9	0						

COMMENTS

Reaction. **(.1) (.2) (.3)** Reaction followed spectrophotometrically and homogeneity proved by packing. Values tabulated in original article in error by factor of ten which is corrected here. Pseudo second order rate law followed throughout 70% of the course. Values of k_1 and k_2 calculated from pseudo second order constants to include dependence of rate upon initial concentration of B. In all cases k_2, the calculated first order constant, was found to fall off at lower pressures although it was reproducible and constant at higher pressures. **(.4)** Occurs simultaneously with reverse reaction, see 311.471. Thermal reaction in dark with equilibrium $Br_2 \rightleftarrows 2Br$ followed by 4.1 as rate controlling step in long chain

$$Cl_3C^{\cdot} + HBr \xrightarrow{k_2} Cl_3CH + Br \text{ and } Cl_3C^{\cdot} + Br_2 \xrightarrow{k_3} Cl_3CBr + Br.$$

$K = k_3/k_2$ also determined by independent kinetic study. Value of K determined by (2) does not agree with value of ~7 calculated by (1) from photo bromination of Cl_3CH at 110 to 130°C. Homogeneity proved by increasing S/V ratio six fold with

COMMENTS *(continued)*

no effect on reaction rate. **(.4.1)** Rate controlling step in (.4) as well as in radioactive exchange, see 301.477.

(.4.2) Competing reactions for intermediate produced in rate controlling step.

LITERATURE

(1) V.V. Braunworth, H.J. Schumacher, *Kolloid Z.* 1939, **89**, 184. (2) R.A. Ogg, *ACS* 1934, **56**, 526. (3) J.H. Sullivan, N. Davidson, *JCP* 1951, **19**, 143.

EXCHANGE

H replacement by halogen on aliphatic C

Reaction type: $RH + X_2 \longrightarrow RX + HX$
(A) (B) (L) (M)

Rate measured: $-dB/dt$

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$CH_4 + Br_2 \longrightarrow CH_3Br + HBr$	$10^3A = 6-15$; $10^4B = 6-15$			$k\,AB^{\frac{1}{2}}(t=0)$	297	7.85	-4					*	(7)
.1.1	$CH_4 + Br \longrightarrow CH_3\cdot + HBr$	(From .1 and photochemical reaction) $k\,AB$				~200				18	2	9		
.1.2	$CH_3\cdot + \begin{cases} HBr \longrightarrow CH_4 + Br & (1) \\ Br_2 \longrightarrow CH_3Br + Br & (2) \end{cases}$	(From .1 and photochemical reaction) $k\,AB$				~200	k_1/k_2			2	2	0		
.2	$C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$	(Only photochemical studies)												(1)
.3	$(CH_3)_3CH + Br_2 \longrightarrow (CH_3)_3CBr + HBr$	$10^3A = 5-15$; $10^4B = 9-26$			$k\,AB^{\frac{1}{2}}(t=0)$	112	9.7	-4					*	(5)
						130	7.6	-3		36				
		$10^3A \sim 8$; $10^3B \sim 1$	M	0.0025	$k\,AB^{\frac{1}{2}}/(1+KM/B)$	130	7.6	-3	4					
.3.1	$(CH_3)_3CH + Br \longrightarrow (CH_3)_3C\cdot + HBr$	(From .3 and photochemical reaction) $k\,AB$								12	4	14		
.3.2	$(CH_3)_3C\cdot + \begin{cases} HBr \longrightarrow (CH_3)_3CH + Br & (1) \\ Br_2 \longrightarrow (CH_3)_3CBr + Br & (2) \end{cases}$	(From .3 and photochemical reaction) $k\,AB$					k_1/k_2			~8		~5		

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$(CH_3)_4C + Br_2 \longrightarrow (CH_3)_3CCH_2Br + HBr$	$10^3A = 5-14$; $10^4B = 5-14$			$k\,AB^{\frac{1}{2}}(t=0)$	197	6.3	-2					*	([6]) ([8])
.4.1	$(CH_3)_4C + Br \longrightarrow (CH_3)_3CCH_2\cdot + HBr$	(From .4 and photochemical reaction)			$k\,AB$	197	3.6	+5		18	9	13	*	([6]) ([8])
										~ 12		~10		([3])
.4.2	$(CH_3)_3CCH_2\cdot + \begin{cases} HBr \longrightarrow (CH_3)_4C + Br & (1) \\ Br_2 \longrightarrow (CH_3)_3CCH_2Br + Br & (2) \end{cases}$	(From .4 and photochemical reaction)			$k\,AB$		k_1/k_2			~ 10		~6		([6]) ([8])
.5	$C_6H_5CH_3 + Br_2 \longrightarrow C_6H_5CH_2Br + HBr$	$10^3A = 4-7$; $10^4B = 4-10$	O_2	0.0003	$k\,AB^{\frac{1}{2}}(t=0)$	166 166	2.9 7	-3 -4					*	([2]) ([10])
.5.1	$C_6H_5CH_3 + Br \longrightarrow C_6H_5CH_2\cdot + HBr$	(From .5 and photochemical reaction)			$k\,AB$	166	8.7	+6		7.6	6	10		([2]) ([10])
.5.2	$C_6H_5CH_2\cdot + \begin{cases} HBr \longrightarrow C_6H_5CH_3 + Br & (1) \\ Br_2 \longrightarrow C_6H_5CH_2Br + Br & (2) \end{cases}$	(From .5 and photochemical reaction)			$k\,AB$		k_1/k_2			5	1	3		([2]) ([10])
.6	$CH_3Br + Br_2 \longrightarrow CH_2Br_2 + HBr$	$10^3A = 6-10$; $10^4B = 7-15$			$k\,AB^{\frac{1}{2}}(t=0)$	297	5.1	-3					*	([7])
.6.1	$CH_3Br + Br \longrightarrow BrCH_2\cdot + HBr$	(From .6 and photochemical reaction)			$k\,AB$	~200				16	2	9		([7])
.7	$Cl_3CH + Br_2 \longrightarrow Cl_3CBr + HBr$	$10^2A = 1.4-4$; $10^4B = 2-38$	M	0-0.037	$k\,AB^{\frac{1}{2}}/(1+KM/B)$	147 169 182	3.01 2.01 5.78	-6 -5 -5	0.0408 0.0403 0.0392	32.0	1.4	11	*	([9]) ([4])
.7.1	$Cl_3CH + Br \longrightarrow Cl_3C\cdot + HBr$	(From .7 and photochemical reaction)			$k\,AB$	147-182				9.3	2.3	9		([9])

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No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.7.2	$Cl_3C\cdot + \begin{cases} HBr \longrightarrow Cl_3CH + Br & (1) \\ Br_2 \longrightarrow Cl_3CBr + Br & (2) \end{cases}$	(From .7 and photochemical reaction) k_1/k_2				147 169 182	4.08 4.03 3.92	-2 -2 -2					*	(9)

COMMENTS

General. Both thermal and photochemical reactions studied, but only thermal rate constants tabulated here. Halogenation assumed to proceed by the same mechanism as that for $H_2 + Br_2 \rightarrow$ see 311.700, with photochemical reaction differing from thermal reaction only in initiating step of the chain: Photochemical,

(1) $Br_2 + h\nu \longrightarrow 2Br$ and thermal,

(1a) $Br_2 + X \longrightarrow 2Br + X$

(2) $Br + RH \longrightarrow R\cdot + HBr$

(3) $R\cdot + Br_2 \longrightarrow RBr + Br$

(4) $R\cdot + HBr \longrightarrow RH + Br$

(5) $2Br + X \longrightarrow Br_2 + X$.

This leads the thermal rate being given by

$$-dB/dt = \frac{k_2(k_1a/k_5)^{\frac{1}{2}}AB^{\frac{1}{2}}}{1 + k_4M/k_3B}$$

Inhibition by HBr observed in all photochemical studies and ratio of rate constants for reactions (4) and (3) determined by varying initial concentration of HBr. Effectiveness of A as third body in recombination reaction (5) varies from a relative value of one for H_2 to 174 for neopentane.

Reaction. **(.1)** Only initial (extrapolated to zero time) rate as reaction followed by (.6) which is almost ten times faster. Inhibition by M studied only for photochemical reaction. Mechanism indicates A to be 1.6 times more effective than H_2 for recombination of Br atoms. **(.3)** Only initial rate (extrapolated to zero time.) Inhibition by M studied for both photochemical and thermal reaction with values of K disagreeing by 50%. It is possible that another competing reaction for $(CH_3)_3C\cdot$ such as $(CH_3)_3C\cdot \longrightarrow$

COMMENTS *(continued)*

$CH_3\cdot$ + $CH_3CH{:}CH_2$ should have been included in the reaction mechanism. Inhibition by oxygen demonstrated. **(.3.2)** Variation in ratio of k_1/k_2 by 50% depending upon whether thermal or photochemical reaction measured. **(.4)** Only initial rate, extrapolated to zero time as rate of further bromination of L not known. Inhibition by M and O_2 demonstrated for the photochemical reaction. Reaction mechanism indicates A to be 174 times more effective than H_2 for recombination of Br atoms. **(.4.1)** Reaction mechanism of (6) (8) did not include competing reaction $(CH_3)_3CCH_2\cdot \longrightarrow CH_3\cdot + (CH_3)_2C{:}CH_2$. Inclusion of this would reduce E to ~12 Kcals. and give normal steric factor according to (3). Product analysis not performed so this has not been confirmed. **(.5)** Only initial rate, extrapolated to zero time. Inhibition by oxygen shown and inhibition by M demonstrated for the photochemical reaction. **(.6)** Only initial rate, extrapolated to zero time, although no appreciable inhibition by M observed and subsequent bromination appeared slow. Mechanism indicates A to be 1.2 times more effective than hydrogen for recombination of Br atoms. **(.7)** Forward and reverse reaction simultaneously as well as independently studied. See 311.417. Homogeneity proved by increasing S/V ratio by factor of 6. **(.7.2)** Ratio of k_1/k_2 of (9) about one third the value reported by (4) at ~120°C but (9) studied both forward and reverse of reaction (.7).

LITERATURE

(1) H.C. Andersen, E.R. Van Artsdalen, *JCP* 1944, **12**, 479. (2) H.R. Anderson, H.A. Scheraga, E.R. Van Artsdalen, *JCP* 1953, **21**, 1258. (3) S.W. Benson, H. Graff, *JCP* 1952, **20**, 1182. (4) V.V. Braunworth, H.J. Schumacher, *Kolloid Z.* 1939, **89**, 184. (5) B.H. Eckstein, H.A. Scheraga, E.R. Van Artsdalen, *JCP* 1954, **22**, 28. (6) E.I. Hormats, E.R. Van Artsdalen, *JCP* 1951, **19**, 778. (7) G.B. Kistiakowski, E.R. Van Artsdalen, *JCP* 1944, **12**, 469. (8) F.E. Schweitzer, E.R. Van Artsdalen, *JCP* 1951, **19**, 1028. (9) J.H. Sullivan, N. Davidson, *JCP* 1951, **19**, 143. (10) E.H. Swegler, H.A. Scheraga, E.R. Van Artsdalen, *JCP* 1951, **19**, 135.

EXCHANGE

Hydrogen - Cyanogen

Hydrogen cyanide formation

Gas phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant		Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	m	E
.1	$H_2 + (CN)_2 \longrightarrow 2\ HCN$	$10^3A = 3.6$;	$10^3B = 3.6$	$k\ AB^{\frac{1}{2}}/[1+m(L/B)]$	575	5.8	-5		
					600	2.0	-4		
					625	5.8	-4	0.25	
					650	1.9	-3		
					675	5.6	-3		72
		1.8	1.8		625	1.5	-3		
		3.6	3.6		"	1.0	-3		
		5.4	5.4		"	8.2	-4		
		5.4	1.8		"	1.2	-3		
		1.8	5.4		"	7.6	-3		

COMMENTS

General. This rate law is taken over from the Bodenstein-Lind kinetics of $H_2 + Br_2$ (see 311.700) and has not been shown to apply to the $H_2 + (CN)_2$ reaction. The above values of k refer to late stages of the reaction; at early stages, k is, roughly, four times as high and falls with the progress of the reaction. Nor is k constant towards variations of A, B. Rate constants calculated on the assumption of a $k\ AB^{\frac{1}{2}}$ law behave in the same way. These data refer to a static system, in a silica vessel; the set of data at 575-675°C was obtained in an aged vessel; the data at 625°C, in a vessel treated with HNO_3. Advance admixture of HCN, in amounts one-half to double the initial $(CN)_2$,

COMMENTS *(continued)*

at 625°C, lowers the rate by a factor of ~0.9. In pyrex at 550°C the rate is about 50% higher than in silica. Surface increase by a factor of 4 increased the rate (in the aged walls) by about 30% at ~600°C but has no appreciable effect at 650-675°C.

LITERATURE

C. N. Robertson, R. N. Pease, *ACS* 1942, **64**, 1810

EXCHANGE

H on Aliphatic C with IInd group metal

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.1	$CH_3COOH + Hg^{++} \longrightarrow$ (products not determined)	CH_3COOH	B = 0.095			$-dB/dt = k B$	50	9.5	-8			*	(1)
							70	1.03	-6				
							90	8.0	-6				
Metal replaced by H on aliphatic C													
.2	$(n\text{-}C_4H_9)_2Hg + CH_3COOH \longrightarrow n\text{-}C_4H_{10} + CH_3COOHgC_4H_9$	CH_3COOH	10^2A = 5-6			$k A$	50	3.76	-5			*	(2)
							75	3.91	-4	20	-16		
.3	$[C_2H_5(CH_3)CH]_2Hg + CH_3COOH \longrightarrow$ $n\text{-}C_4H_{10} + CH_3COOHgCH(CH_3)C_2H_5$	CH_3COOH	10^2A = 5-6			$k A$	25	2.30	-5			*	(2)
							50	1.47	-4				
.4	$[C_6H_5C(CH_3)_2CH_2]_2Hg + CH_3COOH \longrightarrow$ $C_6H_5C(CH_3)_3 + CH_3COOHgCH_2C(CH_3)_2C_6H_5$	CH_3COOH	$10^2A \sim 9$			$k A$	75	1.02	-5			*	(2)
			5	CH_3COONa	0.05		75	9.5	-6				
			5-6		0.0		100	9.35	-5	23	-17		
			6	$HClO_4$	0.022	$k A[HClO_4]$	50	7.0	-3				
			3		0.045		50	6.7	-3				

COMMENTS

Reaction: **(.1)** Appears to involve formation of one C-Hg bond per Hg^{++} reacting. Studied in order to correct for this simultaneous reaction to aromatic mercurations in CH_3COOH. See 312.412. **(.2) (.3) (.4)** Rate law followed up to 85% reaction. Second alkyl mercury bond remaining after 10 to 20 half lives for first bond replacement. In presence of $HClO_4$ oxidation of solvent leads to increase in acidity and separation of metallic mercury after 40-50% reaction.

LITERATURE

(1) H.C. Brown, C.W. McGary, *ACS* 1955, **77**, 2306. (2) S. Winstein, T.G. Traylor, *ACS* 1955, **77**, 3747.

EXCHANGE

H of Aromatic compound with Group II metal

Reaction types:

$$ArH + M^{++} \longrightarrow ArM^{+} + H^{+}$$

$$ArH + RM \longrightarrow ArM + RH$$

$$Ar_2M + AcH \longrightarrow ArH + ArMAc$$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C_6H_6 + Hg^{++} \longrightarrow C_6H_5Hg^{+} + H^{+}$	H_2O	10^2A = 1-4; 10^2B = 2-100	HNO_3	8.0	k AB	25	4.5	-5				*	(6)
				$HClO_4$	3.4		25	7.2	-5					
				$HClO_4$	0.01-0.8	$k = k_o + k_x X$								
				$NaClO_4$	0-0.8	$X = ClO_4^-$								
				$LaClO_4$	0-0.3		40	k_o 2.12	-5					
				ΣClO_4^-	0.06-0.9		40	k_x 3.5	-5					
				HNO_3	0.05-5	$k = k_o + k_x X$								
				$NaNO_3$	0-6	$X = NO_3^-$	40	k_o 2.12	-5					
				ΣNO_3^-	0.1		40	k_x 2.2	-5					
					0.2		40	k_x 2.0	-5					
					0.4		40	k_x 1.5	-5					
					1.2		40	k_x 1.0	-5					
					6.0		40	k_x 1.1	-5					
				Cl^-	0.0	k B	40	2.5	-5					
					0.05		40	1.03	-5					
					0.2		40	2	-7					
		Ac97*	A = 1.0; B = 0.1	$NaClO_4$	0	k AB	25	3.25	-5				*	(6)
					0.20		25	3.40	-5					
					0.40		25	4.34	-5					
					0.60		25	5.35	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.2	$C_6H_6 + Hg(OCOCH_3)_2 \longrightarrow C_6H_5HgOCOCH_3 + CH_3COOH$	M	A = 0.93;			k AB	50	7.5	-7				*	(2)
			B = 0.095				70	5.72	-6					
							90	3.52	-5	22.2	7.6	8		
			A = 0.6-0.9;	$HClO_4$	0.030		25	2.34	-5					
			B = 0.1		0.046		25	3.50	-5					
			A = 0.2-0.6;		0.099		25	7.2	-5					(1)
			B = 0.1											
			A= 2; B= 0.3		0.29		25	1.00	-4					
			A = 0.07-0.4;		0.32		40	8.2	-4					(6)
			B = 0.3											
		Ac97*	A= 1.0; B= 0.1		0		25	4.2	-8				*	(6)
					0.05		25	3.5	-6					
					0.10		25	1.00	-5					
					0.20		25	2.66	-5					
					0.40		25	8.27	-5					
					0.60		25	1.80	-4					
	Mono-alkyl substituted aromatic hydrocarbons													
.3	$CH_3C_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$	M	A = 0.9;			k AB	50	3.77	-6				*	(2)
	$CH_3C_6H_4HgOCOCH_3 + CH_3COOH$		B = 0.09				70	2.47	-5					
							90	1.27	-4	20.3	2.1	8		
			A = 0.6-0.9;	$NaClO_4$	0.09		25	1.28	-6					
			B = 0.09		0.13		25	1.73	-6					
					0.32		25	3.10	-6					
				$HClO_4$	0.030		25	1.58	-4					
					0.046		25	2.50	-4					
			A= 0.1-0.2; B= 0.1		0.098		25	5.59	-4					(1)
			0.4-1	0.09	0.09		25	5.2	-4					
			1.9	0.3	0.28		25	8.0	-4					

Supplement 1955

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$CH_3C_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $o\text{-}CH_3C_6H_4HgOCOCH_3 + CH_3COOH$	M	A = 0.9; B = 0.09			k AB	50	1.16	-6				*	(2)
							70	7.9	-6					
							90	4.14	-5	20.6	1.0	8		
.5	$CH_3C_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $m\text{-}CH_3C_6H_4HgOCOCH_3 + CH_3COOH$	M	A = 0.9; B = 0.09			k AB	50	4.96	-7				*	(2)
							70	3.57	-6					
							90	1.99	-5	21.3	1.3	8		
.6	$CH_3C_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $p\text{-}CH_3C_6H_4HgOCOCH_3 + CH_3COOH$	M	A = 0.9; B = 0.09			k AB	50	2.12	-6				*	(2)
							70	1.32	-5					
							90	6.59	-5	19.9	6	7		
.7	$C_2H_5C_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $C_2H_5C_6H_4HgOCOCH_3 + CH_3COOH$	M	A=0.6; B≃0.1			k AB	50	3.25	-6				*	(3)
.8	$(CH_3)_2CHC_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $(CH_3)_2CHC_6H_4HgOCOCH_3 + CH_3COOH$	M	A=0.6; B≃0.1			k AB	50	3.03	-6				*	(3)
.9	$(CH_3)_3CC_6H_5 + Hg(OCOCH_3)_2 \longrightarrow$ $(CH_3)_3CC_6H_4HgOCOCH_3 + CH_3COOH$	M	A=0.6; B≃0.1			k AB	50	2.48	-6				*	(3)
	Di(tri)(tetra)(penta)-alkyl substituted aromatic hydrocarbons													
.10	$o\text{-}(CH_3)_2C_6H_4 + Hg(OCOCH_3)_2 \longrightarrow$ $(CH_3)_2C_6H_3HgOCOCH_3 + CH_3COOH$	M	A=0.5; B≃0.1			k AB	50	1.26	-5				*	(3)
.11	$m\text{-}(CH_3)_2C_6H_4 + Hg(OCOCH_3)_2 \longrightarrow$ $(CH_3)_2C_6H_3HgOCOCH_3 + CH_3COOH$	M	A=0.5; B≃0.1			k AB	50	2.70	-5				*	(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.12	p-$(CH_3)_2C_6H_4 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_2C_6H_3HgOCOCH_3 + CH_3COOH$	M	A = 0.5; B ≃ 0.1			k AB	50	6.40	-6				*	([3])
.13	1,2,3-$(CH_3)_3C_6H_3 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_3C_6H_2HgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	5.33	-5				*	([3])
.14	1,2,4-$(CH_3)_3C_6H_3 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_3C_6H_2HgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	3.93	-5				*	([3])
.15	1,3,5-$(CH_3)_3C_6H_3 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_3C_6H_2HgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	1.65	-4				*	([3])
.16	1,2,3,4-$(CH_3)_4C_6H_2 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_4C_6HHgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	1.00	-4				*	([3])
.17	1,2,3,5-$(CH_3)_4C_6H_2 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_4C_6HHgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	2.03	-4				*	([3])
.18	1,2,4,5-$(CH_3)_4C_6H_2 + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_4C_6HHgOCOCH_3 + CH_3COOH$	M	A = 0.4; B ≃ 0.1			k AB	50	2.36	-5				*	([3])
.19	$(CH_3)_5C_6H + Hg(OCOCH_3)_2 \longrightarrow (CH_3)_5C_6HgOCOCH_3 + CH_3COOH$	M	A = 0.5; B ≃ 0.1			k AB	50	1.75	-4				*	([3])

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Mono-hydroxy (alkoxy) substituted benzene													
.20	$HOC_6H_5 + Hg^{++} \longrightarrow HOC_6H_4Hg^+ + H^+$	H_2O	A = B = 0.3	HNO_3	5%	k AB	0	5.0	-4				*	(8)
					10%		0	8.3	-4					
					22%		0	1.7	-3					
					34%		0	6.7	-3					
					10%		25	1.33	-2					
	Metal replaced by hydrogen on aromatic-C													
.21	$(C_6H_5)_2Hg + HCOOH \longrightarrow C_6H_6 + HCOOHgC_6H_5$	D10x*	10^2A = 5-10; B = 8.8			k A	29	7.03	-4				*	(5)
			B = 5.5	H_2O	1.4		30	2.7	-4					(4)
			6.6		1.7		30	4.4	-4					
			8.2		6.3		30	1.10	-3					
			9.3		2.4		30	1.14	-3					
.22	$(C_6H_5)_2Hg + CH_3COOH \longrightarrow C_6H_6 + CH_3COOHgC_6H_5$	B	$10^2A \simeq 5$			k A	25	5.14	-4				*	(7)
		D10x*	A = 0.1; B = 8.8				42	2.00	-4				*	(4) (5)
			9.8				42	2.75	-4					
			10.2				42	3.17	-4					
			10.7				42	3.71	-4					
			11.2				42	4.37	-4					
			11.8				42	5.10	-4	18.5	1.3	9		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.23	$(C_6H_5)_2Hg + HClO_4 \longrightarrow C_6H_6 + C_6H_5HgClO_4$	Et95*	10^2A = 1.3-3;			k AB	43	7.23	-3					(5)
			10^2B = 1.6-2				47	1.14	-2					
							50	1.51	-2	21	1	12		
		Di 97.2*					50	3.91	-2					
		Di 96.8*					50	2.97	-2	24	4	14		
		Di 69.5*	10^2A = 1.6;				50	4.84	-3					
			10^2B = 2.7	$KClO_4$	0.0125		50	7.71	-3					
				KCl	0.014		50	5.94	-3					
					0.028		50	7.49	-3					

CODED SOLVENTS

Ac97*	Acetic acid 97% + H_2O
Diox*	Dioxane
Di 97.2(96.8)(69.5)*	Dioxane % indicated + H_2O
Et95*	C_2H_5OH 95% + H_2O

COMMENTS

Reaction. **(.1)** Selected data. Units converted from original minutes. First 10% reaction only. Second order rate constants calculated from measured pseudo first order constants by dividing by saturation concentration of benzene. Solution stirred vigorously and speed of stirring and volume of C_6H_6 did not effect measured rate. Correction made for slight extraction of L from H_2O layer. Rate apparently dependent upon total perchlorate ion and not upon ionic strength or perchloric acid. Similar behavior with sulfuric acid. Slight negative salt effect on catalytic constants of nitrates. Second order rate constants in presence of $(C_2H_5)_4NNO_3$, markedly low, may be due to complexing of C_6H_6 with positive ion, $(C_2H_5)_4N^+$. **(.2)** Second order rate law up to 80% reaction observed by ([1]) indicates polymercuration unimportant. Units converted from original minutes. **(.3)** Only early stages of reaction followed to avoid polymercuration. Rate represents parallel mercuration at all available positions. For reactivity at each position see (.4) (.5) (.6). Reaction followed by titrimetric method for B and by infrared spectra analysis. Units converted from original minutes. **(.4) (.5) (.6)** Units converted from original minutes. Rate constants calculated for these three parallel reactions from total rate (.3) and ratio of products formed. For (.4) (.5) values are twice the partial rate constants per hydrogen of authors and represent the actual rate of formation of ortho and meta compound. **(.7) (.8) (.9) (.10) (.11) (.12) (.13) (.14) (.15 (.16) (.17) (.18) (.19)** Rate law followed from 30-70% reaction. Units converted from original minutes. All rate constants corrected for small parallel reaction with solvent. See 312.421. **(.20)** Units converted from original minutes. Small amount of urea added to remove oxides of nitrogen. **(.21)** Pseudo first order rate constants as B in large excess. Titrimetric method for L and spectrophotometric for A give consistent results. Dilatometric method of ([4]) gives appreciably higher values. **(.22)** Pseudo first order rate constant followed up to 85% reaction and second alkylmercury bond resistant to cleavage up to 20 half lives for first bond. In presence of $HClO_4$ oxidative side reaction occurs with solvent after about 40% reaction which increases acidity and metallic mercury separates. Dilatometric method of ([4]) gives appreciably higher values than titrimetric method for L or spectrophotometric for A.

LITERATURE

(1) H.C. Brown, C.W. McGary, *ACS* 1955, **77**, 2300. (2) H.C. Brown, C.W. McGary, *ACS* 1955, **77**, 2306. (3) H.C. Brown, C.W. McGary, *ACS* 1955, **77**, 2310. (4) A.H. Corwin, M.A. Naylor, *ACS* 1947, **69**, 1004. (5) F. Kaufman, A.H. Corwin, *ACS* 1955, **77**, 6280. (6) R.M. Schramm, W. Klapproth, F.H. Westheimer, *JPC* 1951, **55**, 843. (7) S. Winstein, T.G. Traylor, *ACS* 1955, **77**, 3747. (8) F.H. Westheimer, E. Segel, R. Schramm, *ACS* 1947, **69**, 773.

EXCHANGE
Nitration of Aliphatic Compounds

Liquid phase
Amounts are in M/l.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E
.1	*cyclo*-C_6H_{12} + N_2O_5 $\longrightarrow$ $C_6H_{11}NO_2$, $C_6H_{11}ONO_2$, HNO_3 (L) (M) (N)	CCl_4	A = 0.05–0.4; B = 0.09–0.4	(X) N_2O_4	0.004–0.2	$dL/dt = k\,AB/(0.02 + X^{\frac{1}{2}})$	20	6.4	-5	21.5
						$dM/dt = k\,AB/(0.02 + X^{\frac{1}{2}})$	20	7.1	-5	21.5

COMMENTS

Authors suggest mechanism for reaction involving free radicals but not a chain reaction. The constant 0.02 in the rate law is a measure of the competition between solvent, CCl_4, and NO_2 for reaction with $C_6H_{11}^{\cdot}$. The reaction with CCl_4 leading to formation of $C_6H_{11}Cl$ and oxidation of solvent with formation of CCl_3NO_2 or phosgene. $[C_6H_{11}Cl]/[CCl_3NO_2] = 2.5$.

LITERATURE

J. C. D. Brand, *ACS* 1955, **77**, 2703.

EXCHANGE

Nitration of aromatic compounds

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Coded solvents and coded addends are at the end of the table.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.16	.1	$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$	$M + H_2SO_4$ 68.0 %	$A \ll B = 0.61$			kA	25	2.6	-2				*	(9)
			66.9					25	1.3	-2					
			64.2					25	1.5	-3					
			61.6					25	1.4	-4					
			59.5					25	4.2	-5					
			57.3					25	1.4	-5					
			54.0					25	1.9	-6					
			51.1					25	4	-7					
			CH_3COOH 99.8 %	A = 0.35; B = 12.4	HNO_2	0.5	$k_o = dL/dt$	11	9.7	-4				*	(14)
				0.10 8.0		0.001-0.004	kA	20	1.19	-3					
				0.10 9.7		0.46		20	1.67	-3					
				0.17 9.7		0.46		20	1.35	-3					
				0.21 9.7		0.46		20	1.24	-3					
				0.34 9.7		0.46		20	7.5	-4					
			CH_3NO_2	A = 0.1; B = 3.0	$HNO_2 + H_2SO_4$	0.0034 / 0-0.045	$-dA/dt = k_o + k'[H_2SO_4]$							*	(14)
								-10	$k_o = 1.04$	-6					
								-10	$k' = 1.45$	-3					
.17		$C_6H_6 + N_2O_5 \longrightarrow C_6H_5NO_2 + HNO_3$	CCl_4	A = 2.36; B ~ 0.03	BzOH = C_6H_5COOH; Bz_2O = $(C_6H_5CO)_2O$									*	(11)
				BzOH = 0.063	Bz_2O	0.035	kB	20	2.11	-3					
				"		0.075		20	1.23	-3					
				"		0.144		20	9.35	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.17		$C_6H_6 + N_2O_5 \longrightarrow$ *(continued)*	CCl_4	BzOH = 0.127	Bz_2O	0.035	k B	20	1.07	-3				*	(11)
				0.127		0.102		20	7.74	-4					
.18	.2	$C_6H_5CH_3 + HNO_3 \longrightarrow$	CH_3COOH 99.8 %	A = 0.33; B = 12.4	HNO_2	0.50	$-dA/dt = k_o$	11	1.03	-3				*	(14)
		$CH_3C_6H_4NO_2 + H_2O$		0.05-0.2 7.0		0.002-.006		20	6.3	-5					
			CH_3COOH 90 %	A ≪ B				45	(only relative rate)						(8)
		$\longrightarrow$ 56.5 % (2); 3.5 % (3);	40.0 % (4)		HNO_2 +	0.079									
			CH_3NO_2	A = 0.15; B = 3.0	H_2SO_4	0	k_o	-10	5.3	-7				*	(14)
						0.014		-10	1.28	-6					
						0.042		-10	7.12	-6					
						0.063		-10	1.41	-5					
						0.084		-10	1.86	-5					
				A = 0.09; B = 7.0	HNO_2	0-0.08	$k_o = (a + b[HNO_2]^{\frac{1}{2}})^{-1}$								
							a	-6	8.2	+3					
							b	-6	7.6	+4					
						0.0038	k_o	-6	7.78	-5					
						0.076		-6	3.45	-5					
						0.170		-6	1.84	-5					
						0.420		-6	7.0	-6					
				A ≃ 0.1; B = 7.0	HNO_2 +	0.001-.002	$k_o = a(1 + b[H_2O])^{-1}$								
					H_2O	0-1.6	a	-10	8.8	-5					
							b	-10	1.3	0					
					HNO_2 +	0.0046									
				A = 0.1; B = 7.0	$KClO_4$	0	k_o	-10	9.78	-5					
						0.011		-10	1.03	-4					
					KNO_3	0.0065		-10	6.58	-5					
						0.0123		-10	4.30	-5					
					HNO_2 +	0.001-.002									
					KNO_3	0		-10	8.89	-5					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.18	.2	$C_6H_5CH_3 + HNO_3 \longrightarrow$ *(continued)*	CH_3NO_2	A= 0.1; B= 7.0	HNO_2+ KNO_3	0.001-.002									
						0.0035	k_o	- 10	4.78	-5				*	([14])
						0.023		- 10	2.18	-5					
						0.043		- 10	1.87	-5					
						0.28		- 10	1.30	-5					
						0.63		- 10	9.4	-6					
.19	.3	$C_6H_5C_2H_5 + HNO_3 \longrightarrow$ $C_2H_5C_6H_4NO_2 + H_2O$	CH_3COOH 99.8 %	A= 0.04; B= 7.0	HNO_2	0.0027	$-dA/dt = k_o$	20	6.00	-5				*	([14])
				0.10		0.0046		20	6.20	-5					
				0.10		0.0143		20	5.65	-5					
.20		$C_6H_5C(CH_3)_3 + HNO_3 \longrightarrow$ $(CH_3)_3CC_6H_4NO_2 + H_2O$ $\longrightarrow$ 11.7 % (2); 8.5 % (3); 79.8 % (4)	CH_3COOH 90 %					45	6.4	-1 (rate relative to (.18))					([8])
.21		$C_6H_5OCH_3 + HNO_3 \longrightarrow$ $CH_3OC_6H_4NO_2 + H_2O$	CH_3COOH	A= 0.026; B= 4.93	HNO_2	0.691	k A	21	4.14	-3				*	([7])
			M+H_2SO_4 62.8 %	A ≪ B = 0.61	$(NH_2)_2CO$	0.07	k A	25	3.0	-2					([9])
			59.6					25	4.0	-3					
			57.3					25	9.8	-4					
			53.5					25	1.1	-4					
			49.5					25	1.5	-5					
			45.2					25	2	-6					
			41.3					25	4	-7					
.22		$C_6H_5COOCH_3 + N_2O_5 \longrightarrow$ $CH_3OOCC_6H_4NO_2 + HNO_3$	CCl_4	A= 1.50; B= 0.043			k AB	15	1.34	-3				*	([12])
				1.21				15	1.42	-3					
				0.83				15	1.53	-3					
				0.64				15	1.63	-3					
				→0				15	1.82	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.23		$C_6H_5COOC_2H_5 + HNO_3 \longrightarrow C_2H_5OOCC_6H_4NO_2 + H_2O$	CH_3COOH 99.8 %	A= 0.10; B= 10.5	HNO_2	0.0029	k A	20	1.55	-4					(14)
.24		$C_6H_5COOC_2H_5 + N_2O_5 \longrightarrow C_2H_5OOCC_6H_4NO_2 + HNO_3$	CCl_4	A = 1.35;			k AB	15	1.44	-3				*	(12)
				1.08				15	1.53	-3					
				0.80				15	1.70	-3					
				0.55				15	1.87	-3					
				→0				15	2.17	-3					
			$CHCl_3$	0.5				20	4.41	-3					
				B = 0.03-.05											
.25		$C_6H_5COOC(CH_3)_3 + N_2O_5 \longrightarrow (CH_3)_3COOCC_6H_4NO_2 + HNO_3$	CCl_4	A = 1.07;			k AB	15	2.07	-3				*	(12)
				0.73				15	2.38	-3					
				0.57				15	2.54	-3					
				→0				15	3.02	-3					
				B = 0.04-.06											
.26		$C_6H_5CH_2SO_3Na + HNO_3 \longrightarrow NaSO_3CH_2C_6H_4NO_2 + H_2O$ $\longrightarrow$ 14 % (3)	M + H_2SO_4 18.7 mol %	A= 0.164; B= 7.0 mol %			k A	40	3.33	-4					(13)
.27		$C_6H_5CH_2CH_2SO_3Na + HNO_3 \longrightarrow NaSO_3CH_2CH_2C_6H_4NO_2 + H_2O$	M + 17.2 mol % B	A = 0.169		Mol %	k A							*	(13)
					$NaClO_4$	0.00		30	2.48	-3					
						0.32		30	2.80	-3					
						0.57		30	3.15	-3					
						1.06		30	3.93	-3					
					$NaNO_3$	0.63		30	2.22	-3					
						1.09		30	2.13	-3					
						2.12		30	1.87	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.27		$C_6H_5CH_2CH_2SO_3Na + HNO_3 \longrightarrow$													
		(continued) Mol % M	Mol % $HClO_4$	Mol % B; A = 0.169		mol ratio	k A							*	([13])
		75.5	7.8	16.7	M/B =	82/18		30	1.16	-4					
		75.1	8.3	16.6		"		30	2.68	-4					
		74.0	9.6	16.4		"		30	7.48	-4					
		73.4	10.3	16.3		"		30	1.45	-3					
		73.0	10.9	16.1		"		30	3.00	-3					
		76.6	7.7	15.7	$M/HClO_4$	90.8/9.2		30	9.9	-5					
		74.1	7.5	18.4		"		30	2.33	-4					
		72.7	7.4	19.9		"		30	4.30	-4					
		71.3	7.2	21.5		"		30	7.18	-4					
		69.7	7.1	23.2		"		30	1.87	-3					
		67.8	6.8	25.4		"		30	4.80	-3					
		76.5	11.3	12.2		87.2/12.8		30	4.32	-4					
		74.9	11.0	14.1		"		30	9.33	-4					
		73.5	10.8	15.7		"		30	1.97	-3					
		72.5	10.6	16.9		"		30	3.30	-3					
		72.6	10.2	17.2				20	8.15	-4					
		"	"	"				30	2.48	-3					
		"	"	"				40	6.22	-4	17.4	8	9		
		73.8	9.8	16.4; A = 0.08				25	4.53	-4					([6])
		73.8	9.8	16.4 0.84				25	2.30	-4					
		60.0	0	40.0 0.53			$-dA/dt = k_o$	0	1.07	-4					
.28		$C_6H_5C{:}N + HNO_3 \longrightarrow$	M + H_2SO_4 85.0 %	A << B = 0.61			k A	25	9.0	-3				*	([9])
		$NCC_6H_4NO_2 + H_2O$	84.0					25	3.5	-3					
			83.0					25	1.5	-3					
			82.0					25	5.1	-4					
			81.0					25	1.9	-4					
			80.0					25	1.0	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.29		$C_6H_5N(CH_3)_3^+ + HNO_3 \longrightarrow$	$M + H_2SO_4$ 100 %	A = 0.05; B = 0.03			k AB	25	8.1	-3	~16			*(3)	(10)
		m-$(CH_3)_3N^+C_6H_4NO_2 + H_2O$	100	0.30 0.03				25	1.2	-2					
			100	0.50 0.03				25	1.4	-2					
			100	2.5 0.03				25	1.19	-2					
			100	A = B = 0.025				25	8.5	-3					
			99.5	"				25	9.3	-3	~15	1	9		
			98.3	"				25	1.18	-2					
			96.6	"				25	1.57	-2					
			96.6	A = 0.025; B = 0.05-0.07				25	1.64	-2					
			96.6	0.10				25	1.59	-2					
			94.7	A = B = 0.025				25	2.16	-2					
			91.0	"				25	3.48	-2					
			88.4	"				25	2.66	-2					
			87.5	"				25	1.65	-2	13.4	1.0	8		
			86.5	"				25	7.43	-3					
			85.9	"				25	4.78	-3					
			84.7	"				25	1.76	-3					
			82.0	"				25	1.71	-4					
			$H_2SO_4 + SO_3$ 2.8 %					25	9.5	-3					(10)
			5.5					25	1.13	-2					
			7.5					25	1.33	-2					
			10.3					25	1.53	-2					
.30	.8	$C_6H_5NO_2 + HNO_3 \longrightarrow$	B	A = 0.20	HNO_2	0.001-0.2	k A; $k = (a + b[HNO_2]^{\frac{1}{2}})^{-1}$							*	(14)
		$C_6H_4(NO_2)_2 + H_2O$					a	-13	1.7	+2					
							b	-13	2.5	+2					
			B + M 3 %	A = 0.21; M = 1.65	HNO_2	0.1-0.26	k A; $k = (a + b[HNO_2]^{3/2})^{-1}$								
							a	-13	3.0	+2					
							b	-13	2.5	+4					

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
							$kA;\ k = (a + b[HNO_2]^{3/2})^{-1}$								
.30	.8	$C_6H_5NO_2 + HNO_3 \longrightarrow$	B + M 5 %	A = 0.20; M = 2.93	HNO_2	0.001-0.3	a	-13	5.0	+2				*	(14)
		(continued)					b	-13	4.0	+4					
			B + M	A = 0.07-0.1; M = 0	HNO_2	0.040	kA	-13	4.68	-3					
				0.40		"		-13	3.54	-3					
				0.89		"		-13	2.76	-3					
				2.10		"		-13	1.57	-3					
				3.19		"		-13	7.7	-4					
				0.02 2.5	HNO_2+	0.02									
					KNO_3	0.0		-13	6.00	-3					
						0.11		-13	5.32	-3					
						0.21		-13	4.11	-3					
						0.32		-13	2.96	-3					
			$M + H_2SO_4$ 97.4 %	A = 0.05-0.1; B = 0.03			kAB	25	1.58	-2					(4) (5)
			86.7					25	2.23	-2					
.31		$C_6D_5NO_2 + HNO_3 \longrightarrow$	$M + H_2SO_4$ 97.4 %	A = 0.05-0.1; B = 0.03			kAB	25	1.57	-2				*	(4)
		$C_6D_4(NO_2)_2 + DOH$	86.7					25	2.14	-2					
.32	.4	$C_6H_5F + HNO_3 \longrightarrow$	$M + H_2SO_4$ 70.0 %	A << B = 0.61			kA	25	1.3	-2				*	(9)
		$FC_6H_4NO_2 + H_2O$	68.4					25	7.0	-3					
			68.0					25	4.0	-3					
			66.4					25	9.9	-4					
			64.4					25	2.0	-4					
			62.8					25	5.3	-5					
			59.6					25	8	-6					
			54.0					25	4	-7					
			CH_3COOH 99.8 %	A = 0.1-0.2; B = 8.0	HNO_2	0.004	kA	20	2.6	-4				*	(14)
				9.0		0.004		20	1.1	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.33	.5	$C_6H_5Cl + HNO_3 \longrightarrow$	$M + H_2SO_4$ 72.0 %	$A \ll B = 0.61$			$k\,A$	25	4.7	-2				*	(9)
		$ClC_6H_4NO_2 + H_2O$	70.0					25	7.7	-3					
			68.4					25	3.0	-3					
			68.0					25	1.7	-3					
			64.4					25	8.4	-5					
			62.8					25	2.7	-5					
			59.6					25	2.5	-6					
			57.0					25	7	-7					
			CH_3COOH 99.8 %	A = 0.10; B = 9.0	HNO_2	0.0043	$k\,A$	20	5.2	-4				*	(14)
				0.05 10.0		0.0022		20	3.65	-3					
				0.10 10.0		0.0022		20	3.25	-3					
				0.23 10.0		0.0022		20	2.94	-3					
				0.30 10.0		0.0022		20	2.81	-3					
				0.10 10.0		0.101		20	1.19	-3					
				0.10 10.0		0.135		20	6.14	-4					
				0.10 10.0		0.160		20	4.18	-4					
				0.10 10.0		0.203		20	1.50	-4					
				0.10 10.0		0-0.08	$k\,A;\ k = (a + b[HNO_2]^{\frac{1}{2}})^{-1}$								
							a	20	2.40	+2					
							b	20	1.47	+3					
.34	.6	$C_6H_5Br + HNO_3 \longrightarrow$	$M + H_2SO_4$ 72.0 %	$A \ll B = 0.61$			$k\,A$	25	4.5	-2				*	(9)
		$BrC_6H_4NO_2 + H_2O$	70.0					25	7.3	-3					
			68.4					25	2.7	-3					
			68.0					25	1.60	-3					
			64.4					25	7.2	-5					
			62.8					25	2.3	-5					
			59.6					25	3	-6					
			57.0					25	7	-7					
			CH_3COOH 99.8 %	A = 0.10; B = 9.0	HNO_2	0.0043	$k\,A$	20	4.5	-4				*	(14)
				0.20 9.0		0.0043		20	3.9	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.35	.7	$C_6H_5I + HNO_3 \longrightarrow$ $IC_6H_4NO_2 + H_2O$	CH_3COOH 99.8 %	A = 0.1-0.2; B = 8.0 9.0	HNO_2	0.004 0.0043	k A	20 20	2.8 1.37	-4 -3				*	(14)
		Di-substituted-benzene													
.36		p-$(CH_3)_2C_6H_4 + HNO_3 \longrightarrow$ $(CH_3)_2C_6H_3NO_2 + H_2O$	CH_3COOH 99.8 %	A = 0.01; B = 7.0 0.07 7.0 0.06 5.0	HNO_2	0.0046 0.0192 0.0096	$dL/dt = k_o$	20 20 20	6.17 5.70 4.33	-5 -5 -6				*	(14)
.37		p-$CH_3C_6H_4COOCH_3 + N_2O_5 \longrightarrow$ $CH_3C_6H_3(COOCH_3)NO_2 + HNO_3$	CCl_4	A = 1.1; B = 0.03 0.9 0.06 0.6 0.03 → 0			k AB	15 15 15 15	1.58 1.81 1.86 2.18	-3 -3 -3 -3				*	(12)
.38		o-$(C_2H_5OOC)_2C_6H_4 + N_2O_5 \longrightarrow$ $(C_2H_5OOC)_2C_6H_3NO_2 + HNO_3$	CH_3CN CH_3NO_2 $CH_3NO_2 + CCl_4$ vol. ratio = 9:1 7:3 5:5 1:9	A = 1.1; B = 0.05 0.8 0.05 0.8 0.05 0.8 0.05 0.8 0.05 0.59 0.06 0.74 0.05 0.90 0.05 1.20 0.05			k AB	20 20 20 20 20 20 20 20 20	2.9 3.07 2.70 2.27 2.02 1.40 1.43 1.39 1.31	-3 -3 -3 -3 -3 -3 -3 -3 -3				*	(12)
.39		p-$CH_3C_6H_4N(CH_3)_3^+ + HNO_3 \longrightarrow$ 3-NO_2-4-$CH_3C_6H_3N(CH_3)_3^+ + H_2O$	$M + H_2SO_4$ 81.7 % 75.8	A = B = 0.1			k AB	25 25	1.08 4.07	-1 -4	13.7 17.6	2 8	8 9	*(16) (20)	

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.40	$o\text{-}NO_2C_6H_4OH + HNO_3 \longrightarrow$	M + B 30 %	10^3A = 3.1	HNO_2	0.031	k A	0	8	-7				*	([19])
	$(NO_2)_2C_6H_3OH + H_2O$		3.1		0.031		50	1.15	-3					
			3.1		0.0054		50	2.5	-4					
			2.8		0.0010		50	1.15	-4					
			0.56		0.0011		50	1.35	-4					
		20 %	3.1		0.031		50	2.5	-4					
		10 %	3.1		0.031		50	3	-5					
.41	$p\text{-}NO_2C_6H_4OH + HNO_3 \longrightarrow$	M + B 60 %	10^3A = 3.1	HNO_2	0.081	k A	30	9.2	-4					([19])
	$(NO_2)_2C_6H_3OH + H_2O$	"	"		0.030		30	4.3	-4					
		"	"		0.0048		30	6.3	-5					
		"	"		0.0022		30	3.5	-5					
		"	"		0.0007		30	1.00	-5					
		50 %	"		0.031		0	1.5	-6					
		"	"		0.048		30	2.8	-4					
		"	"		0.031		50	1.8	-4					
		"	"		0.017		50	1.3	-4					
		"	"		0.0037		50	5.0	-5					
		"	"		0.0017		50	2.0	-5					
		40 %	"		0.031		30	7	-5					
		30 %	"		0.031		20	2.3	-5					
		"	"		0.143		30	3.8	-4					
		"	"		0.031		30	2.3	-4					
		"	"		0.0058		30	8.8	-5					
		20 %	"		0.031		50	3.8	-5					
		10 %	"		0.031		50	6.8	-6					
		CH_3COOH	10^2A = 2-4; B = 4.6	HNO_2	0.1-1.8	k A$[HNO_2]$	21	2.2	-3				*	([7])
			10^2A = 2.5; B = 3.35		0.56		21	2.8	-3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.41	p-$NO_2C_6H_4OH + HNO_3 \longrightarrow$ *(continued)*	CH_3COOH	$10^2A = 2.5$; $B = 2.70$	HNO_2	0.55	$k\,A[HNO_2]$	21	3.1	-3				*	(7)
			1.38		0.38		21	3.6	-3					
			$B = 1.4$-5.8		0.1-1.8	$k = a - b[HNO_3]$								
						a	21	4.2	-3					
						b	21	4.5	-4					
			$10^2A = 2.5$; $B = 10$	HNO_2	0.1	k_1A	21	1.30	-2					
					0.5-1.0		21	5.0	-3					
.42	p-$ClC_6H_4OCH_3 + HNO_3 \longrightarrow$ 4-Cl-2-$NO_2C_6H_3OCH_3 + H_2O$	CH_3COOH	$A = 0.08$; $B = 4.44$	N_2O_4	0.0375	$k\,A$	35	2.61	-3				*	(2)
				N_2O_4	0.01-0.03	$k = [N_2O_4](k_2 + k_3K/[NO_3^-])$								
				$(CH_3)_4NNO_3$	0.007-0.08	k_2	35	1.3	-2					
				$(C_2H_5)_4NNO_3$	0.01-0.02	k_3K	35	2.5	-4					
			$10^2A = 3$-8; $B = 4.14$	HNO_2	0-0.34	$k\,A[HNO_2]$	25	5.2	-3				*	(7)
			$10^2A = 6$; $B = 4.2$	$HNO_2 + LiNO_3$	0.04-0.08									
					0		35	1.59	-2					
					0.040		35	1.33	-2					
					0.081		35	1.03	-2					
					0.16		35	1.24	-2					
					0.24		35	1.45	-2					
					0.38		35	1.77	-2					
			$10^2A = 6$; $B = 4.1$	$HNO_2 + KNO_3$	0.1-0.16									
					0		35	1.40	-2					
					0.055		35	1.27	-2					
					0.076		35	1.22	-2					
					0.114		35	1.12	-2					
					0.152		35	1.09	-2					
					0.228		35	1.18	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.42	p-$ClC_6H_4OCH_3 + HNO_3 \longrightarrow$ *(continued)*	CH_3COOH	$10^2A = 6$; $B = 4.1$	$HNO_2 + H_2O$		$k\,A[HNO_2]$							*	([7])
					0		35	1.31	-2					
					0.11		35	1.21	-2					
					0.22		35	1.11	-2					
					0.44		35	1.01	-2					
					0.89		35	0.93	-2					
					1.11		35	0.94	-2					
			$10^2A = 5$; $B = 5.94$	HNO_2	0-0.14	$k_1A + k\,A[HNO_2]$								
						k_1	25	1.8	-4	(see comments)				
						k	25	5.8	-2					
			$10^2A = 2$; $B = 9.05$	HNO_2	3.5×10^{-4}	$dL/dt = k_o$	-15	9.1	-6					
					7.5×10^{-4}		-15	9.6	-6					
					0		-11	2.2	-5					
					0		-5	3.5	-5					
					2.5×10^{-4}		-5	2.4	-5					
					5.5×10^{-4}		-5	2.0	-5					
					9.5×10^{-4}		-5	1.7	-5					
.43	m-$ClC_6H_4COOC_2H_5 + N_2O_5 \longrightarrow$ $Cl\text{-}NO_2C_6H_3COOC_2H_5 + HNO_3$	CCl_4	$A = 0.6-1$; $B = 0.04-0.06$			$k\,AB$	15	8.7	-4				*	([12])
.44	p-$ClC_6H_4N(CH_3)_3^+ + HNO_3 \longrightarrow$ $Cl\text{-}NO_2C_6H_3N(CH_3)_3^+ + H_2O$	$M + H_2SO_4$ 99.4 %	$A = B = 0.025$			$k\,AB$	25	1.53	-3				*	([10])
		98.4					25	2.10	-3	17.4	1.6	-8		
		95.8					25	3.42	-3	17.0	1.6	-8		
		93.1					25	4.82	-3					
		90.8					25	5.80	-3	16.3	7	-9		
		88.4					25	3.86	-3					
		$H_2SO_4 + SO_3$ 0.52%					25	1.40	-3					
		2.87					25	1.63	-3	17.5	1.1	-8		
		4.21					25	1.78	-3					
		6.21					25	1.95	-3	15.8	1.1	-9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.45	$p\text{-}ClC_6H_4NO_2 + HNO_3 \longrightarrow$	B	A = 0.15	HNO_2	0.03	k A	20	1.37	-5					(14)
	$ClC_6H_3(NO_2)_2 + H_2O$	$M + H_2SO_4$ 97.4 %	A = 0.05; B = 0.03			k AB	25	1.74	-3				*	(4) (5)
		95.6	0.02 0.02				25	3.52	-3					(5) (19)
		92.0	0.02 0.02				25	5.48	-3					
		90.0	0.01 0.01				25	6.85	-3					
		86.7	0.05 0.03				25	2.37	-3					(4) (5)
		$H_2SO_4 + SO_3$ 0.0 %	A = B = 0.025				25	9.6	-4				*	(10)
		2.80					25	4.9	-4					
		5.38					25	3.4	-4					
		10.93					25	1.90	-4					
		14.6					25	1.26	-4					
		19.7					25	6.7	-5					
.46	$o\text{-}Cl_2C_6H_4 + HNO_3 \longrightarrow$	CH_3COOH 99.8 %	A = 0.10; B = 10.5	HNO_2	0.0029	k A	20	2.57	-4					(14)
	$Cl_2C_6H_3NO_2 + H_2O$													
.47	$o\text{-}Cl_2C_6H_4 + N_2O_5 \longrightarrow$	CCl_4	A = 1.42; B = 0.043			k AB	15	7.71	-4				*	(12)
	$Cl_2C_6H_3NO_2 + HNO_3$		1.11 0.043				15	8.03	-4					
			0.88 0.043				15	8.19	-4					
			0.61 0.043				15	8.25	-4					
			→0 0.043				15	8.5	-4					
.48	$m\text{-}Cl_2C_6H_4 + HNO_3 \longrightarrow$	CH_3COOH 99.8 %	A = 0.10; B = 10.5	HNO_2	0.0029	k A	20	4.98	-4					(14)
	$Cl_2C_6H_3NO_2 + H_2O$													
.49	$m\text{-}Cl_2C_6H_4 + N_2O_5 \longrightarrow$	CCl_4	A = 0.6-1; B = 0.06			k AB	15	1.21	-3				*	(12)
	$Cl_2C_6H_3NO_2 + HNO_3$													

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.50	$p\text{-}Cl_2C_6H_4 + HNO_3 \longrightarrow$	CH_3COOH 99.8 %	A= 0.10; B= 10.5	HNO_2	0.0029	k A	20	2.00	-4				*	(14)
	$Cl_2C_6H_3NO_2 + H_2O$		12.0		0.0030		10	6.76	-4					
			12.0		0.0030		20	1.65	-3					
			12.2		0.0034		20	2.23	-3					
		CH_3NO_2	A= 0.1-0.2; B= 8.5	HNO_2	0.0018	k A	20	6.49	-3					
					0.048		20	2.55	-3					
					0.083		20	1.87	-3					
					0.106		20	1.00	-3					
					0.174		20	4.5	-4					
					0-0.08	$k = (a + b[HNO_2]^{\frac{1}{2}})^{-1}$								
						a	20	4.0	+1					
						b	20	1.6	+3					
			A= 0.1; B= 8.5;	HNO_2 +	0.008									
			M= 0.3	KNO_3	0	k A	20	6.49	-3					
					0.010		20	3.48	-3					
					0.025		20	1.93	-3					
					0.061		20	1.11	-3					
					0.081		20	9.7	-4					
.51	$p\text{-}Cl_2C_6H_4 + N_2O_5 \longrightarrow$	CCl_4	A= 0.5-0.8; B= 0.05			k AB	10	3.1	-4				*	(12)
	$Cl_2C_6H_3NO_2 + HNO_3$		0.7-1.9 0.04-.06				15	5.4	-4					
			0.5-1.8 0.04				20	9.6	-4	17	1	10		
			A≃0.6; B≃0.04	HNO_3	0-0.25	k AB; $k = a + b[HNO_3]^2$							*	(12)
						a	20	1.1	-3					
						b	20	8.0	-3					
		CT/NM 9*	A= 1.78; B= 0.055			k AB	10	5.79	-4					
			1.28 0.040				10	6.67	-4					
			0.58 0.047				10	8.04	-4					
			→0 ~0.05				10	9.04	-4					

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.51	p-$Cl_2C_6H_4 + N_2O_5 \longrightarrow$	CT/NM 9*	A = 1.28; B = 0.05			k AB	15	1.18	-3				*	(12)
	$Cl_2C_6H_3NO_2 + HNO_3$		0.63 0.05				15	1.36	-3					
	(continued)		→0 0.05				15	1.65	-3					
			0.63 0.05				20	2.49	-3					
			→0 0.05				20	2.65	-3					
		CT/NM 9*	A≃0.8; B≃0.05	TEAP*	0	k AB	10	7.99	-4					
					1.8×10^{-3}		10	1.25	-3					
					2.5×10^{-3}		10	2.28	-3					
					4.0×10^{-3}		10	3.06	-3					
				TEAHS*	0		20	2.44	-3					
					4.6×10^{-4}		20	3.26	-3					
					1.2×10^{-3}		20	4.31	-3					
				TEAN*	0		25	3.39	-3					
					4.5×10^{-4}		25	3.75	-3					
					6.0×10^{-4}		25	4.48	-3					
		CT/NM 7*	A = 1.30; B = 0.038			k AB	10	1.08	-3					
			0.97				10	1.24	-3					
			0.64				10	1.50	-3					
			→0				10	1.85	-3					
			0.71 0.06-0.1				20	4.3	-3					
.52	p-$ClC_6H_4Br + N_2O_5 \longrightarrow$	CCl_4	A = 0.5-1.2; B = 0.04			k AB	15	5.5	-4				*	(12)
	$Cl,BrC_6H_3NO_2 + HNO_3$													
.53	p-$C_6H_4Br_2 + N_2O_5 \longrightarrow$	CCl_4	A = 0.4-0.7; B = 0.04			k AB	15	5.7	-4				*	(12)
	$Br_2C_6H_3NO_2 + HNO_3$													

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
		Tri-substituted Benzene													
.54		$1,3,5\text{-}(CH_3)_3C_6H_3 + HNO_3 \longrightarrow (CH_3)_3C_6H_2NO_2 + H_2O$	CH_3COOH 99.8 %	A = 0.05-0.1; B = 7.0	HNO_2	0.004	$dL/dt = k$	20	5.62	-5					(14)
						0.007		20	5.48	-5					
				A = 0.07; B = 5.0		0.014		20	4.17	-6					
.55		$3,5\text{-}(CH_3)_2C_6H_3CH_2SO_3^- + HNO_3 \longrightarrow SO_3^-CH_2\text{-}(CH_3)_2C_6H_2NO_2 + H_2O$	M + B Mol % =	39.2; A = 0.11			k_1A	0	4.60	-3				*	(6)
				39.7 0.23			$dL/dt = k_o$	0	1.81	-4					
				38.9 0.32				0	1.47	-4					
				17.6 0.07	$HClO_4$	6.6 Mol %	k_1A	25	5.9	-4					
				17.6 0.19				25	3.8	-4					
.56	.12	$2,4\text{-}(NO_2)_2C_6H_3CH_3 + HNO_3 \longrightarrow (NO_2)_3C_6H_2CH_3 + H_2O$	H_2SO_4 100 %	A ≃ 0.4; B ≃ 0.2			$k\,AB$	70	1.88	-5				*	(1)
								80	4.68	-5					
								90	1.23	-4	23.4	1.4	10		
				≃0.6 ≃0.8				90	1.8	-4					
			$M + H_2SO_4$ 98.7 %	≃0.4 ≃0.2				90	1.78	-4					
			95.0					60	1.68	-5					
								80	1.28	-4					
				0.4 0.1				90	2.9	-4					
				0.2				90	3.1	-4					
				0.4				90	3.2	-4					
				0.6				90	3.4	-4					
				≃0.4 ≃0.2				100	7.1	-4					
								120	3.9	-3	23.5	4.7	10		
			93.0					90	3.74	-4					
			92.0					90	4.02	-4					
			91.0					90	3.50	-4					
			89.5					70	4.34	-5					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.56	.12	2,4-$(NO_2)_2C_6H_3CH_3$ + HNO_3 →	M + H_2SO_4 89.5%	A≃0.4; B≃0.2			k AB	90	2.82	-4				*	(1)
		$(NO_2)_3C_6H_2CH_3$ + H_2O						110	1.40	-3	22.6	1.0	11		
			87.4					90	1.15	-4					
		(continued)	H_2SO_4 + SO_3 7.8 %					70	1.3	-5					
								80	3.7	-5					
								90	9.4	-5	24.2	3	10		
			11.7					90	9.0	-5					
			16.6					90	8.2	-5					
.57		2,4-$(NO_2)_2C_6H_3OH$ + HNO_3 →	M + B 50 %	A = 0.0012	HNO_2	0.026	k A	50	7	-7				*	(20)
		$(NO_2)_3C_6H_2OH$ + H_2O													
.58		2,6-$(NO_2)_2C_6H_3OH$ + HNO_3 →	M + B 50 %	A = 0.001	HNO_2	0.027	k A	50	2.3	-5				*	(20)
		$(NO_2)_3C_6H_2OH$ + H_2O	60			0.0065		50	1.7	-5					
						0.029		50	5.7	-5					
						0.108		50	1.8	-4					
.59		1-$NO_2C_6H_3$:$(CO)_2$:C_6H_4 + HNO_3 →	B	A = 0.24	HNO_2	0.0055	k A	20	2.48	-3				*	(14)
				H_2SO_4 = 0.044;	"	0.0085		20	2.53	-3					
				0.101	"	0.0090		20	3.09	-3					
				0.176	"	0.0065		20	4.19	-3					
				0.234	"	0.0070		20	5.03	-3					
.60		1,2,4-$Cl_3C_6H_3$ + HNO_3 →	CH_3COOH 99.8 %	A= 0.10; B= 12.2	HNO_2	0.0034		20	1.80	-4				*	(14)
		$Cl_3C_6H_2NO_2$ + H_2O	CH_3NO_2	A= 0.10; B= 8.5		0.0018		20	5.44	-4					
.61		1,2,4-$Cl_3C_6H_3$ + N_2O_5 →	CT/NM 9*	A= 0.55; B= 0.049			k AB	15	6.82	-4				*	(12)
		$Cl_3C_6H_2NO_2$ + HNO_3		0.70				15	6.19	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.61	$1,2,4\text{-}Cl_3C_6H_3 + N_2O_5 \longrightarrow$ *(continued)*	CT/NM 9*	A = 1.20; B = 0.049			k AB	15	5.80	-4				*	(12)
			0.71 0.049				20	1.23	-3	17		~10		
			0.82 0.043				20	1.07	-3					
			1.15				20	1.00	-3					
		CT/NM 7*	A → 0				20	2.47	-3					
		CT/NM 5*	→ 0				20	2.76	-3					
	Tetra-substituted benzene													
.62	$2,4,6\text{-}(CH_3)_3C_6H_2CH_2SO_3^- + HNO_3 \longrightarrow$ $SO_3^-CH_2\text{-}(CH_3)_3C_6H\ NO_2 + H_2O$	M + B Mol % =	37.4; A = 0.29			$dL/dt = k_o$	0	1.09	-4				*	(6)
			39.4 0.27				0	1.60	-4					
			39.4 0.17			k_1A	0	7.26	-3					

SOLVENTS

CT/NM 9*	9 vol CCl_4 + 1 vol CH_3NO_2
CT/NM 7*	7 vol CCl_4 + 3 vol CH_3NO_2
CT/NM 5*	1 vol CCl_4 + 1 vol CH_3NO_2

ADDENDS

TEAP*	Tetra ethyl ammonium picrate
TEAHS*	Tetra ethyl ammonium hydrogen sulfate
TEAN*	Tetra ethyl ammonium nitrate

COMMENTS

Reaction. **(.16)** Pseudo first order rate constants measured by ([9]) as nitric acid in excess. Concentrations of benzene listed by ([9]) not true concentrations but refer to optical densities. In acetic acid at concentrations of nitric acid <12, mixed order observed by ([14]) with initial reaction being pseudo zero order tending to first order in latter stages. Zero order only at high nitric acid concentrations where large addition of HNO_2 necessary to depress rate to measurable value. HNO_2 shown by ([14]) to have no effect on reaction order. In CH_3NO_2 linear catalysis by H_2SO_4 only when $[H_2SO_4]>[HNO_2]$. **(.17)** Active nitrating species considered by ([11]) to be N_2O_5 which is involved in the following rapid equilibria: $Bz_2O + N_2O_5 \rightleftharpoons 2BzNO_3$; $BzOH + N_2O_5 \rightleftharpoons BzNO_3 + HNO_3$; $Bz_2O + HNO_3 \rightleftharpoons BzNO_3 + BzOH$. First equilibrium is catalyzed by acid. Only in extremely pure Bz_2O is this equilibrium slower than the rate of nitration. Under these conditions nitration is so rapid that even the BzO_2 is nitrated. In a mixture rate is comparable to rate using $BzNO_3$. **(.18)** Pseudo zero order over entire course in contrast to (.16). In CH_3NO_2 linear catalysis by H_2SO_4 only when $[H_2SO_4]>[HNO_2]$. Reciprocal of zero order rate constant linear with respect to $[HNO_2]^{\frac{1}{2}}$ up to $[HNO_2] = 0.08$. At higher concentrations reciprocal of rate constant increases more rapidly. Reciprocal of zero order rate constant linear with respect to $[H_2O]$ over range studied. Initial concentration of H_2O used rather than average. **(.19)** Pseudo zero order over entire course in contrast to (.16). **(.21)** In CH_3COOH rate law pseudo first order only when sufficient HNO_2 present initially. Side reaction leading to dark colored products making up at least 10% of yield cause autocatalysis by the HNO_2 produced. Order with respect to HNO_2 varies with concentration of HNO_3 going from 0.65 when $[HNO_3] = 3.0$ to 0.2 when $[HNO_3] = 6.0$. In H_2SO_4 pseudo first order as HNO_3 in excess. Values of concentration of $CH_3OC_6H_5$ listed by ([9]) are not actually concentrations but functions of optical density. **(.22)** **(.24)** **(.25)** Second order rate constants calculated from pseudo first order initial rate constants dividing by concentration of N_2O_5. At latter stages reaction shows autocatalysis by HNO_3 produced. Selected data. **(.27)** Selected data from large amount by ([13]). Relatively small depression of rate constants by NO_3^- considered to be caused by canceling of major effect by a large positive salt effect. ([6]) observe initial rate to tend toward zero order followed by a limiting first order reaction. Addition of $NaNO_3$ de-

COMMENTS *(continued)*

presses both zero and first order rate constants to the same extent. Addition of $NaClO_4$ increases first order rate constant more than it increases zero order constant. **(.28)** Pseudo first order as HNO_3 in excess. Values of concentrations of C_6H_5CN listed by ([9]) are not actual concentrations but functions of optical density. **(.29)** Rate constants converted to seconds from original minutes. **(.30)** Addition of water tremendously increases the inhibiting effect of HNO_2 and changes it from a $\frac{1}{2}$ power effect in anhydrous media, to a $\frac{3}{2}$ power of $[HNO_2]$. **(.31)** Lack of any measurable isotope effect shows that the rate determining step is not the removal of hydrogen. **(.32) (.33) (.34)** Rate constants pseudo first order as HNO_3 in excess. Concentrations of C_6H_5F listed by ([9]) are not actual concentrations but functions of optical density. Selected data of ([14]) who observe slight decrease in calculated first order constants with increase in initial concentration of C_6H_5F. **(.35)** Slight decrease in calculated first order constants observed with increase in initial concentration of A. **(.36)** Rate law is zero order over entire course of reaction in contrast to (.16) which is mixed first and second order and (.32)-(.35) which approach first order over entire course in this solvent. **(.37) (.38)** Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A which was in excess. At latter stages reaction shows autocatalysis by HNO_3 produced. **(.39)** Rate constants are in seconds converted from original minutes. **(.40)** Selected data. Rate constants converted to seconds from original minutes. **(.41)** Rate constants converted to seconds from original minutes of ([19]). In CH_3COOH ([7]) observed first order dependence upon HNO_2 up to $[HNO_3] = 5.0$ but some inhibiting effect of HNO_2 observed at $[HNO_3] = 10.0$. The linear dependence of the calculated second order constants upon $[HNO_3]$ from 1.4-5.8 considered to be due to a partial balancing of strong effects. **(.42)** In CH_3COOH ([2]) deduce dependence of pseudo first order rate constant k upon $[N_2O_4]$ and $[NO_3^-]$ as $k = [N_2O_4](k_2 + k_3K/[NO_3^-])$ where k_2 is rate constant for nitrosation by N_2O_4 and k_3 for nitrosation by NO^+. Nitrosation is assumed to be followed by the rapid reaction $ArNO + HNO_3 \longrightarrow ArNO_2 + HNO_2$. k_2 determined from intercept of graph $k_2 = 1.3 \times 10^{-2}$. A lower limit for k_3 estimated from graph and upper limit for:

$$K = 1.9 \times 10^{-3} = [NO_3^-][NO^+]/[N_2O_4].$$

k_3 lower limit = 0.13. At $[HNO_3] = 5.94$ the rate law of

COMMENTS *(continued)*

([7]), $k_1A + kA[HNO_2]$ is not valid at $[HNO_2] = 0$. In absence of HNO_2 reaction is nearly zero order with respect to A. At $[HNO_3]$ in the range 6-9 M/l the kinetics are complicated having fractional non-constant reaction orders. At $[HNO_3]$ = 9-10 simple orders are again observed if $[HNO_2]$ is not too large. Above $[HNO_3]$ = 10 M/l the reaction is too fast to measure. **(.43)** Second order rate constants calculated from initial pseudo first order constants by dividing by the concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. **(.44)** Rate constants converted to seconds from original minutes. **(.45)** Rate constants in H_2O-H_2SO_4 calculated by combining relative rates of ([5]) with rate constants for (.30) of ([4]) and ([19]). **(.47) (.49)** Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. **(.50)** Reciprocal of rate constant linear with respect to $[HNO_2]^{\frac{1}{2}}$ only up to $[HNO_2]$ = 0.08. At higher concentrations the reciprocal of the rate constant increases more rapidly. Excellent first order behavior over 97% reaction in CH_3NO_2 observed by ([14]). This is in contrast to (.16) (.18) and (.19) where zero order behavior over the reaction course is found for this solvent. **(.51) (.52) (.53)** Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. **(.55)** Initial rate of reaction tends to zero order. This is followed by a limiting first order reaction. Addition of $NaNO_3$ depresses both first and second order rate constants to the same extent. Addition of $NaClO_4$ increases first order rate constant much more than it increases the zero order constant. **(.56)** Selected data. Rate constants in all H_2SO_4 media given by:

$$k = \{k_1 [HSO_4^-] + k_2 [H_2SO_4] + k_3 [H_2S_2O_7^-]\} Q$$

where $Q = [NO_2^+]/[HNO_3] = \{1 + [OH_3^+][HSO_4^-]^2/33[H_2SO_4]^2\}^{-1}$ at 90°C. $10^5 k_1 = 5.5$; $10^6 k_2 = 6.2$; $10^6 k_3 = 9.3$. Value of k_3 is in doubt as $[HS_2O_7^-]$ in oleum is uncertain. In excess SO_3, Q approaches 1. Rate constants converted to seconds from original minutes. **(.57) (.58)** Rate constants converted to seconds from original minutes. **(.59)** Selected data. **(.60)** In CH_3NO_2 good first order rate through 97% reaction in contrast to zero order in this solvent for (.16) (.18) and (.19). **(.61)** Second order rate constants calculated by dividing initial pseudo first order constants

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COMMENTS *(continued)*

by concentration of A. At latter stages the reaction shows autocatalysis by HNO_3 formed. (.62) Initial rate of reaction tends to zero order. This is followed by a limiting first order reaction. Addition of $NaNO_3$ depresses both first and zero order rate constants to the same extent. Addition of $NaClO_4$ increases the first order rate constant much more than it increases the zero order constant.

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EXCHANGE

Aryl Hydrogen substitution by Azo

(Diazocoupling reactions)

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec^{-1}.

Note: For compounds involving more than one aromatic ring, it is understood that the substitution take place in the ring written last. The position of substitution in the product, *if given*, is designated by a position number after the arrow counted in the same order as in the reactant.

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$CH_3COCH_2CONHC_6H_5 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		6.4	*k* AB	15	1.13	0				*	(5)
			$10^4B = 2$			6.7		15	2.67	0					
						7.0		15	5.53	0					
.2	$CH_3COCH_2CONHC_6H_5 + 3\text{-}NO_2C_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		5.0	*k* AB	15	1.65	+1				*	(5)
			$10^4B = 2$			5.4		15	4.09	+1					
.3	$CH_3COCH_2CONHC_6H_5 + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		5.62	*k* AB	15	3.91	0				*	(5)
			$10^4B = 2$			6.12		15	2.32	+1					
.4	$1,3\text{-}(HO)_2C_6H_4 + 3\text{-}CH_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		5.82	*k* AB	15	1.13	0				*	(5)
			$10^4B = 2$			6.04		15	1.88	0					
						6.26		15	3.97	0					
						6.48		15	7.90	0					
.5	$1,3\text{-}(HO)_2C_6H_4 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		6.0	*k* AB	15	4.40	-1				*	(5)
			$10^4B = 2$			6.4		15	1.26	0					
						6.8		15	3.83	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.6	$1,3\text{-}(HO)_2C_6H_4 + 2\text{-}CH_3OC_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		5.82	k AB	15	1.57	-1				*	([5])
			$10^4B = 2$			6.25		15	6.12	-1					
						6.66		15	2.22	0					
						6.88		15	4.47	0					
.7	$1,3\text{-}(HO)_2C_6H_4 + 4\text{-}CH_3OC_6H_4N_2^+ \longrightarrow$	H_2O	$10^3A = 2$;	Buffers		6.58	k AB	15	4.55	-1				*	([5])
			$10^4B = 2$			6.80		15	9.92	-1					
						7.00		15	2.08	0					
.8	$1,3\text{-}(HO)_2C_6H_4 + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^4A = 1\text{-}5$	Buffers	0.24	4.50	k AB	15	1.97	0				*	([4])
			$10^3A = 2$;			5.0		15	4.90	0				*	([5])
			$10^4B = 2$			5.2		15	8.80	0					
			$10^4A = 1\text{-}5$		0.24	5.27		15	1.35	+1					([4])
			$10^3A = 2$;			5.4		15	1.52	+1					([5])
			$10^4B = 2$												
.9	$4\text{-}HOC_6H_4SO_3Na + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow$	H_2O	$10^4A = 1\text{-}5$	Buffers	0.24	8.17	k AB	15	1.1	-1				*	([4])
						9.15		15	5.3	-1					
	Mono-substituted napthalene														
.10	$C_{10}H_7\text{-}2\text{-}OH + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^3A = 2$;	Buffers		6.4	k AB	15	1.54	0				*	([5])
			$10^4B = 2$			6.6		15	2.17	0					
						7.0		15	6.13	0					
						7.4		15	1.62	+1					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Di-substituted napthalenes														
.11	1-HO-3-$HSO_3C_{10}H_6$ + 2-$NO_2C_6H_4N_2^+$ ⟶ (2), (4)	H_2O	$10^5A = 5$; $10^5B = 1$	Acetate buffers	0.5	4.59	k AB	20	3.09	+5				*	(7)
						4.61		20	4.00	+5					
						4.64		20	5.39	+5					
						5.60		20	5.04	+5					
	" " ⟶ (2)					4.59	k_o AB	20	2.9	+5					
						5.60		20	4.2	+5					
	" " ⟶ (4)					4.59	k_p AB	20	2.1	+4					
						5.60		20	8.8	+2					
.12	1-HO-3-$HSO_3C_{10}H_6$ + 4-$ClC_6H_4N_2^+$ ⟶ (2) ~75%, (4) ~25%	H_2O	$10^5A = 5$; $10^5B = 1$	Phosphate buffers	0.25	6.35	k AB	10	1.66	+3					(6)
.13	1-HO-3-$HSO_3C_{10}H_5$-2-D + 4-$ClC_6H_4N_2^+$ ⟶ ⟶ (2) ~80%, (4) ~20%	H_2O	$10^5A = 5$; $10^5B = 1$	Phosphate buffers	0.25	6.35	k AB	10	5.35	+2					(6)
.14	1-OH-4-$NaSO_3C_{10}H_6$ + $C_6H_5N_2^+$ ⟶ (2)	H_2O	$10^4A = 1-5$; $10^4B = 1-5$	Buffers	0.24	5.27	k AB	15	5.9	-1				*	(4)
						5.80			2.10	0					
.15	1-OH-4-$NaSO_3C_{10}H_6$ + p-$CH_3C_6H_4N_2^+$ ⟶ (2)	H_2O	$10^4A = 1-5$; $10^4B = 1-5$	Buffers	0.24	6.30	k AB	15	1.58	0				*	(4)
						6.73		15	4.70	0					
.16	1-HO-4-$HSO_3C_{10}H_6$ + 2-$CH_3OC_6H_4N_2^+$ ⟶ (2)	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers + KCl	.005	5.7	k AB	10	4.6	-2					(12)
					.01	5.7		10	4.5	-2					
					.02	5.7		10	4.6	-2					
					.05	5.7		10	3.7	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.16	$1\text{-HO-4-HSO}_3\text{C}_{10}\text{H}_6 + 2\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2) *(continued)*	H_2O	$10^3A = 1$;	Buffers +	.10	5.7	*k* AB	10	3.2	-2					(12)
			$10^5B = 1$	KCl	.25	5.7		10	2.8	-2					
			$10^4A = 5-10$;		.24	5.80		15	1.37	-1				*	(4)
			$10^4B = 5$		.24	6.30		15	5.09	-1					
					.24	6.73		15	1.22	0					
					.24	7.08		15	2.64	0					
					.24	5.80		25	3.28	-1	15	3	10		
					.24	6.30		25	1.28	0					
					.24	6.73		25	3.08	0	16	2	12		
.17	$1\text{-HO-4-HSO}_3\text{C}_{10}\text{H}_6 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2)	H_2O	$10^3A = 1$;	Buffers +	.005	5.7	*k* AB	10	7.2	0					(12)
			$10^5B = 1$	KCl	.01	5.7		10	7.4	0					
					.02	5.7		10	8.0	0					
					.05	5.7		10	8.1	0					
					.10	5.7		10	8.9	0					
					.25	5.7		10	9.8	0					
.18	$1\text{-HO-4-NaSO}_3\text{C}_{10}\text{H}_6 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2)	H_2O	$10^4A = 5$;	Buffers	0.24	4.50	*k* AB	15	1.85	0				*	(4)
			$10^4B = 1-5$			4.94		15	5.08	0					
						5.27		15	1.10	+1					
						4.50		25	4.45	0	15	4	11		
.19	$1\text{-HO-4-HSO}_3\text{C}_{10}\text{H}_6 + 4\text{-ClC}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2)	H_2O	$10^5A = 5$;	Phosphate	0.25	6.35	*k* AB	10	4.06	+2					(6)
			$10^5B = 1$	buffers											
.20	$1\text{-HO-4-HSO}_3\text{C}_{10}\text{H}_5\text{-2-D} + 4\text{-ClC}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2)	H_2O	$10^5A = 5$;	Phosphate	0.25	6.35	*k* AB	10	3.95	+2					(6)
			$10^5B = 1$	buffers											
.21	$1\text{-HO-5-H}_2\text{NSO}_2\text{C}_{10}\text{H}_6 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$ (2)	H_2O	$10^3A = 2$;	Buffers		6.4	*k* AB	15	1.33	0				*	(5)
			$10^4B = 2$			6.7		15	2.53	0					
						7.0		15	4.26	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.22	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + \text{C}_6\text{H}_5\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^2A = 1$; $10^5B = 1$	Buffers	0.25	4.61	k AB	20	7.40	+2				*	(10)
.23	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + 3\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.25	6.34	k AB	20	2.86	+2				*	(10)
.24	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.005	7.0	k AB	10	1.02	0					(12)
					0.01	7.0		10	1.00	0					
					0.02	7.0		10	9.5	-1					
					0.05	7.0		10	9.3	-1					
					0.10	7.0		10	8.0	-1					
					0.25	7.0		10	7.1	-1					
					0.25	6.34		20	1.68	+2				*	(10)
			$10^4A = 1\text{-}100$; $10^5B = 1$		0.25	5.09		20	2.75	-2					(13)
					0.25	5.71		20	1.01	-1					
					0.25	6.24		20	4.04	-1					
					0.25	6.71		20	1.05	0					
					0.25	7.18		20	3.10	0					
.25	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + 3\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^2A = 1$; $10^5B = 1$	Buffers	0.25	4.61	k AB	20	1.20	+3				*	(10)
.26	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^2A = 1$; $10^5B = 1$	Buffers	0.25	6.34	k AB	20	3.35	+1				*	(10)
.27	$2\text{-HO-6-HSO}_3\text{C}_{10}\text{H}_6 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.005	7.0	k AB	10	4.8	+1				*	(12)
					0.01	7.0		10	5.0	+1					
					0.02	7.0		10	5.1	+1					
					0.05	7.0		10	5.7	+1					
					0.10	7.0		10	6.3	+1					
					0.25	7.0		10	6.3	+1					

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.28	2-HO-6-$HSO_3C_{10}H_6$ + 3-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.25	4.61	k AB	20	1.07	+4				*	([10])
.29	2-HO-6-$HSO_3C_{10}H_6$ + 4-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^4A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	3.35	+3				*	([10])
.30	2-HO-6-$HSO_3C_{10}H_6$ + 2,5-$(HSO_3)_2C_6H_3N_2^+$ ⟶ (1)	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.005	7.0	k AB	10	4.8	0					([12])
					0.01	7.0		10	5.1	0					
					0.02	7.0		10	6.0	0					
					0.05	7.0		10	8.3	0					
					0.10	7.0		10	1.26	+1					
					0.25	7.0		10	1.91	+1					
.31	2-HO-8-$HSO_3C_{10}H_6$ + 4-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 1$; $10^4B = 1$	Buffers	0.25	6.35	k AB	10	7.4	0					([6])
.32	2-HO-8-$HSO_3C_{10}H_5$-1-D + 4-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 1$; $10^4B = 1$	Buffers	0.25	6.35	k AB	10	1.2	0					([6])
.33	1-NH -4-$HSO_3C_{10}H_6$ + 4-$HSO_3C_6H_4N_2^+$ ⟶ (2)	H_2O	A:B = (2-5)	Buffers	0.24	2.04	k AB	25	6.6	-1				*	([8])
					0.24	3.43		25	1.0	0					
					0.24	3.49		25	2.8	0					
					0.24	4.51		25	2.3	0					
					0.24	5.18		25	2.3	0					
.34	1-NH_2-8-$HSO_3C_{10}H_6$ + $C_6H_5N_2^+$ ⟶ (2)	H_2O	A:B = (2-5)	Buffers	0.24	2.43	k AB	25	5.2	-1				*	([8])
					0.24	3.49		25	6.9	0					
					0.24	4.32		25	1.1	+1					
					0.24	4.95		25	3.3	+1					
					0.24	6.25		25	5.0	+1					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.35	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + C_6H_5N_2^+ \longrightarrow (1)$	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	2.24	0				*	(10)
.36	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 3\text{-}CH_3C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	8.5	-1				*	(10)
.37	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^3A = 1$; $10^5B = 1$	Buffers	0.005	5.70	k AB	10	2.55	-1					(9)
					0.01	5.69		10	2.35	-1					
					0.02	5.67		10	2.19	-1					
					0.05	5.62		10	1.94	-1					
					0.10	5.58		10	1.66	-1					
					0.25	5.53		10	1.59	-1					
			$10^4A = 1\text{-}100$;		0.25	5.09		20	3.22	-1					(13)
			$10^5B = 1$		0.25	5.60		20	3.3	-1				*	(10)
					0.25	7.18		20	3.84	-1	12				(13)
.38	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 3\text{-}CH_3OC_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^4A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	4.80	0				*	(10)
.39	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 4\text{-}CH_3OC_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^2A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	7.80	-2				*	(10)
.40	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 3\text{-}NO_2C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^4A = 1$; $10^5B = 1$	Buffers	0.25	2.09	k AB	20	2.0	+3				*	(10)
.41	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 4\text{-}NO_2C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.25	2.09	k AB	20	2.24	+3				*	(10)
.42	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.005	5.72	k AB	10	6.81	+1					(9)
					0.01	5.71		10	6.74	+1					
					0.02	5.70		10	6.81	+1					
					0.05	5.67		10	6.67	+1					
					0.10	5.63		10	6.85	+1					
					0.25	5.60		10	6.87	+1					
					0.25	5.60		20	1.05	+2	7			*	(10)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.43	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 3\text{-}ClC_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.25	5.60	k AB	20	8.78	+1				*	([10])
.44	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 4\text{-}ClC_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^4A = 1$	Buffers	0.25	5.60	k AB	20	1.64	+1				*	([10])
.45	$2\text{-}NH_2\text{-}6\text{-}HSO_3C_{10}H_6 + 2,5\text{-}(HSO_3)_2C_6H_3N_2^+ \longrightarrow (1)$	H_2O	$10^5A = 1$; $10^5B = 1$	Buffers	0.005	5.72	k AB	10	4.50	+1					([9])
					0.01	5.71		10	4.69	+1					
					0.02	5.70		10	5.08	+1					
					0.05	5.67		10	5.50	+1					
					0.10	5.63		10	6.00	+1					
					0.25	5.60		10	6.25	+1					
					0.25	5.60		20	8.42	+1	5	3	5	*	([10])
	Tri-substituted napthalene														
.46	$1\text{-}OH\text{-}3,8\text{-}(NaSO_3)_2C_{10}H_5 + C_6H_5N_2^+ \longrightarrow (2)$	H_2O	$10^4B = 1\text{-}5$; $A \gtrless B$	Buffers	0.24	6.30	k AB	15	1.35	-1				*	([4])
						7.08		15	8.36	-1					
.47	$1\text{-}OH\text{-}3,8\text{-}(NaSO_3)_2C_{10}H_5 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow (2)$	H_2O	$10^4B = 1\text{-}5$; $A \gtrless B$	Buffers	0.24	7.08	k AB	15	3.28	-1				*	([4])
						8.17		15	3.33	0					
.48	$1\text{-}OH\text{-}3,8\text{-}(NaSO_3)_2C_{10}H_5 + 2\text{-}CH_3OC_6H_4N_2^+ \longrightarrow (2)$	H_2O	$10^4B = 1\text{-}5$; $A \gtrless B$	Buffers	0.24	7.08	k AB	15	9.3	-2				*	([4])
						8.17		15	1.04	0					
.49	$1\text{-}OH\text{-}3,8\text{-}(NaSO_3)_2C_{10}H_5 + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow (2)$	H_2O	$10^4B = 1\text{-}5$; $A \gtrless B$	Buffers	0.24	4.94	k AB	15	1.58	-1				*	([4])
						5.80		15	1.30	0					
.50	$1\text{-}OH\text{-}3,8\text{-}(NaSO_3)_2C_{10}H_5 + 4\text{-}BrC_6H_4N_2^+ \longrightarrow (2)$	H_2O	$10^4B = 1\text{-}5$; $A \gtrless B$	Buffers	0.24	5.27	k AB	15	5.3	-1				*	([4])
						5.80		15	1.78	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.51	2-OH-3,6-$(NaSO_3)_2C_{10}H_5$ + $C_6H_5N_2^+$ ⟶ (2)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	5.27	k AB	15	1.75	-1				*	(4)
						5.80		15	5.95	-1					
.52	2-OH-3,6-$(NaSO_3)_2C_{10}H_5$ + 4-$CH_3C_6H_4N_2^+$ ⟶ (1)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	5.80	k AB	15	2.12	-1				*	(4)
						6.73		15	2.75	0					
.53	2-OH-3,6-$(NaSO_3)_2C_{10}H_5$ + 2-$CH_3OC_6H_4N_2^+$ ⟶ (1)	H_2O	10^4A= 1-5; 10^5B= 1-5	Buffers	0.24	6.3	k AB	15	2.08	-1				*	(4)
						7.08		15	1.23	0					
						7.08		25	3.4	0	17	1	13		
.54	2-OH-3,6-$(NaSO_3)_2C_{10}H_5$ + 4-$HSO_3C_6H_4N_2^+$ ⟶ (1)	H_2O	10^4A= 1-5; 10^4B= 1-5	Buffers	0.24	4.94	k AB	15	6.64	-1				*	(4)
						5.27		15	1.61	0					
						5.80		15	5.50	0					
						5.27		25	3.75	0	15	4	11		
.55	2-OH-3,6-$(NaSO_3)_2C_{10}H_5$ + 4-$BrC_6H_4N_2^+$ ⟶ (1)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	5.27	k AB	15	1.08	0				*	(4)
						5.80		15	3.70	0					
.56	2-OH-6,8-$(NaSO_3)_2C_{10}H_5$ + $C_6H_5N_2^+$ ⟶ (1)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	7.08	k AB	15	5.32	-2				*	(4)
						8.17		15	5.64	-1					
.57	2-OH-6,8-$(NaSO_3)_2C_{10}H_5$ + 4-$CH_3C_6H_4N_2^+$ ⟶ (1)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	8.17	k AB	15	2.64	-1				*	(4)
						9.15		15	1.20	0					
.58	2-OH-6,8-$(NaSO_3)_2C_{10}H_5$ + 4-$HSO_3C_6H_4N_2^+$ ⟶ (1)	H_2O	10^4B= 1-5; A⇌B	Buffers	0.24	6.30	k AB	15	1.16	-1				*	(4)
						7.08		15	5.92	-1					
.59	2-OH-6,8-$(HSO_3)_2C_{10}H_5$ + 4-$NO_2C_6H_4N_2^+$ ⟶ (1)	H_2O	10^4A= 1; 10^5B= 1	Buffers		6.65	k AB	10	1.55	+3					(11)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.60	2-OH-6,8-$(HSO_3)_2C_{10}H_4$-1-D + 4-$NO_2C_6H_4N_2^+$ ⟶ (1)	H_2O	$10^4A = 1$; $10^5B = 1$	Buffers		6.65	k AB	10	3.24	+2					([11])
.61	2-OH-6,8-$(HSO_3)_2C_{10}H_5$ + 3-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 2$; $10^5B = 1$	Buffers		7.28	k AB	10	1.07	+1					([11])
.62	2-OH-6,8-$(HSO_3)_2C_{10}H_4$-1-D + 3-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 2$; $10^5B = 1$	Buffers		7.28	k AB	10	1.95	0					([11])
.63	2-OH-6,8-$(HSO_3)_2C_{10}H_5$ + 4-$ClC_6H_4N_2^+$ ⟶ (1)	H_2O	$10^3A = 2$-1; $10^5B = 1$	Buffers		6.69	k AB	10	6.2	-1					([11])
			$10^4A = 5$-20			6.85		10	1.54	0					
			Base catalyst	[Base]											
			C_5H_5N	.0234		6.66	k AB	10	6.03	0					
				.0467		6.64		10	1.10	+1					
				.0931		6.63		10	2.24	+1					
				.140		6.62		10	2.95	+1					
				.232		6.60		10	4.68	+1					
				.463		6.60		10	8.01	+1					
				.687		6.54		10	1.02	+2					
				.911		6.51		10	1.15	+2					
			2-$CH_3C_5H_4N$	.0215		7.16		10	4.79	0					
				.0897		7.31		10	1.29	+1					
				.221		7.25		10	2.82	+1					
				.433		7.18		10	4.37	+1					
			3-$CH_3C_5H_4N$	.0228		7.14		10	8.32	0					
				.0914		7.14		10	2.57	+1					
				.225		7.08		10	5.50	+1					
				.441		6.99		10	8.25	+1					
			4-$CH_3C_5H_4N$	.0217		7.25		10	1.10	+1					
				.0897		7.39		10	3.47	+1					
				.222		7.34		10	7.41	+1					
				.438		7.28		10	1.10	+2					

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.63	$2\text{-OH-6,8-}(HSO_3)_2C_{10}H_5 + 4\text{-}ClC_6H_4N_2^+ \longrightarrow (1)$ *(continued)*	H_2O	*Base* catalyst	[Base]								(11)
			$2,6\text{-}(CH_3)_2C_5H_3N$	.0171		7.01	k AB	10	1.32	0		
				.0364		7.05		10	2.11	0		
				.0739		7.07		10	3.60	0		
				.145		7.04		10	6.40	0		
				.205		6.95		10	8.69	0		
				.267		6.92		10	1.15	+1		
.64	$2\text{-OH-6,8-}(NaSO_3)_2C_{10}H_5 + 4\text{-}BrC_6H_4N_2^+ \longrightarrow (1)$	H_2O	$10^4B = 1\text{-}5$; $A \rightleftharpoons B$	Buffers	0.24	5.80	k AB	15	9.40	-2	*	(4)
						6.73		15	6.00	-1		
	Heterocyclic aromatic											
.65	$\overline{NHCH{:}CHN{:}CH} + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow 4\text{-}HSO_3C_6H_4N_2\overline{C{:}NCH{:}CHNH} + H^+$	H_2O	$10^4A = 1\text{-}10$; $10^5B = 1\text{-}5$	Buffers		7.10	k AB	25	3.0	-1	*	(3)
						8.15		25	1.20	0		
						9.15		25	9.1	0		
						10.0		25	3.52	+1		
						11.0		25	4.69	+1		
.66	$\overline{C_6H_4CH{:}CHNH} + 4\text{-}NO_2C_6H_4N_2^+ \longrightarrow \overline{C_6H_4NHCH{:}C}\text{-}N_2C_6H_4\text{-}4\text{-}NO_2 + H^+$ (indole)	H_2O	$10^4A = 1\text{-}10$; $10^5B = 2\text{-}5$	Buffers		4-6	k AB	0	2.3	0		(1)
						6.7		0	3.1	0		
						7.6		0	3.9	0		
						8.6		0	5.2	0		
						9.2		0	4.5	0		
.67	$\overline{C_6H_4CD{:}CHNH} + 4\text{-}NO_2C_6H_4N_2^+ \longrightarrow \overline{C_6H_4NHCH{:}C}\text{-}N_2C_6H_4\text{-}4\text{-}NO_2 + D^+$ (indole-D-substitute)	H_2O	$10^4A = 5$; $10^5B = 3$	Buffers		6.7	k AB	0	3.36	0		(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.68	$\overline{C_6H_4CHN{:}NH} + p\text{-}HSO_3C_6H_4N_2^+ \longrightarrow$ (3) (indazole)	H_2O	10^3A = 2-10; 10^4B = 2-20	Buffers		8.50	k AB	25	1.0	-2	*	([2])
						8.65		25	1.0	-2		
						9.00		25	1.8	-2		
						9.15		25	5.0	-2		
						9.60		25	1.4	-1		
						10.10		25	4.6	-1		
.69	$\overline{C_6H_4CHN{:}NN{:}NC_6H_4SO_3H} + 4\text{-}HSO_3C_6H_4N_2^+ \longrightarrow$	H_2O	10^3A = 0-10; 10^4B = 2-20	Buffers		8.5	k AB	25	8 ± 3	0	*	([2])
						9.0		25	5	0		
						9.6		25	7	0		
						10.1		25	8	0		
.70	$\overline{C{:}ONHN{:}C(CH_3)}CH_2 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow \overline{C{:}ONHN{:}C(CH_3)}CHN_2C_6H_4CH_3 + H^+$ (3-methyl-5-pyrazolone)	H_2O	10^3A = 2; 10^4B = 2	Buffers		5.4	k AB	15	8.90	-1	*	([5])
						6.2		15	5.43	0		
						6.6		15	1.17	+1		
.71	$\overline{C{:}ON(C_6H_5)N{:}C(CH_3)}CH_2 + 2\text{-}CH_3C_6H_4N_2^+ \longrightarrow$ (4) (3-methyl-1-phenyl-5-pyrazolone)	H_2O	10^3A = 2; 10^4B = 2	Buffers		4.52	k AB	15	1.43	0	*	([5])
						4.70		15	2.43	0		
						4.89		15	3.60	0		
						5.12		15	5.72	0		
.72	$\overline{C{:}ON(C_6H_5)N{:}C(CH_3)}CH_2 + 3\text{-}CH_3C_6H_4N_2^+ \longrightarrow$ (4) (3-methyl-1-phenyl-5-pyrazolone)	H_2O	10^3A = 2; 10^4B = 2	Buffers		4.15	k AB	15	1.48	0	*	([5])
						4.36		15	2.45	0		
						4.53		15	4.08	0		
						4.76		15	7.10	0		
.73	$\overline{C{:}ON(C_6H_5)N{:}C(CH_3)}CH_2 + 4\text{-}CH_3C_6H_4N_2^+ \longrightarrow$ (4) (3-methyl-1-phenyl-5-pyrazolone)	H_2O	10^3A = 2; 10^4B = 2	Buffers		4.6	k AB	15	2.47	0	*	([5])
						5.0		15	5.92	0		
						5.4		15	1.40	+1		

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.74	$\overline{C{:}ON(C_6H_5)N{:}C(CH_3)}CH_2 + 2\text{-}CH_3OC_6H_4N_2^+ \longrightarrow (4)$ (3-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3A = 2$; $10^4B = 2$	Buffers		4.53	k AB	15	1.38	0	*	([5])
						5.06		15	4.47	0		
						5.31		15	8.33	0		
.75	$\overline{C{:}ON(C_6H_5)N{:}C(CH_3)}CH_2 + 4\text{-}CH_3OC_6H_4N_2^+ \longrightarrow (4)$ (3-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3A = 2$; $10^4B = 2$	Buffers		5.2	k AB	15	1.90	0	*	([5])
						5.4		15	3.33	0		
						5.6		15	5.55	0		

COMMENTS

General. In most of the coupling reactions listed, pseudo first order rate constants were determined with diazonium ion in smaller amount. Second order rate constants were calculated by dividing pseudo first order constants by analytical concentration of reactant in excess. In some cases authors also divided pseudo first order constants by calculated concentration of supposed reactive species. Such values have not been tabulated except where so stated under comments. Diazo coupling reactions are listed in order of the compound undergoing coupling, substituted benzene derivatives being listed first followed by mono-substituted napthalene, then di- and tri-substituted napthalene derivatives. These are followed by heterocyclic substances. In each group the compound with OH precedes NH_2, NO_2, HSO_3^-, Cl^-, Br^-, and I^-. Compounds with substituents in the 1-position precede, 2, 3, 4 etc. The diazonium ions are also arranged in a corresponding order.

Literature. ([4]) Units of rate constants converted to seconds from original minutes. A to B ratio varied from $\frac{1}{5}$ to 5. Plot of log of rate constant vs. pH observed to be linear with slope of unity. ([5]) Units converted to seconds from original minutes. Amperometric method used. Buffers used were Clark and Luba. Plot of log of rate constant vs. pH linear but slope varied from 0.6 to 1.3. ([5]) points out that similar plot by ([4]) had slope 0.9 not unity. ([8]) Units converted to seconds from original minutes. Concentrations of reactants not stated by authors. pH dependence concluded to indicate coupling involves diazonium ion with free amine.

COMMENTS *(continued)*

Reaction. **(.6)** Rate constant converted to seconds from original minutes. Reaction followed potentiometrically. Authors calculate rate constants for paths involving $HOC_6H_4O^-$ and $OC_6H_4O^=$ ions. **(.9)** Calculated second order rate constants decreased with progress of reaction in this alkaline medium. Values approximate. **(.11)** Authors studied in detail influence of temperature, base catalysis and reaction medium upon ortho and para coupling. **(.22)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 98.8%. **(.23)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield of product of coupling 82.2%. **(.24)** Rate constant at 20°C by ([10]) corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 69.5%. **(.25)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 88.1%. **(.26)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 92.1%. **(.28)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 89.2%. **(.29)** Rate constant corrected for side reaction and calculated in terms of naptholate ion as reactant. Yield 89.2%. **(.33) (.34)** Units converted to seconds from assumed minutes. **(.35)** Rate constant corrected for side reaction. Yield of product of coupling 89%. **(.36)** Rate constant corrected for side reaction. Yield of product of coupling 88%. **(.37)** Rate constant of ([10]) corrected for side reaction. Yield of product of coupling 75.5%. Approximate value for activation energy calculated by editor. **(.38)** Rate constant corrected for side reaction. Yield of product of coupling 89.8%. **(.39)** Rate constant corrected for side reaction. Yield of product of coupling 82.8%. **(.40)** Rate constant corrected for side reaction. Yield of coupled product 73.7%. **(.41)** Rate constant corrected for side reaction. Yield of coupled product 68.1%. **(.42)** Rate constant of ([10]) corrected for side reaction. Yield of coupled product 67.3%. Approximate value for activation energy calculated by editor. **(.43)** Rate constant corrected for side reaction. Yield of coupled product 84.4%. **(.44)** Rate constant corrected for side reaction. Yield of coupled product 89.6%. **(.45)** Activation energy and frequency factor of doubtful accuracy as based on only two values ten degrees apart. ([10]) corrected rate constant for side reactions. Yield of coupled product 71%. **(.65)** Authors show reactive species is probably anion of A since plot of its concentration vs. pH has same shape as plot of rate constant vs. pH. **(.68)** Rate constant corrected for simultaneous zero order decomposition of B with $10^9 k_0$ = 0.6, 9.0, 20.0, 5.0, 1.0 and 25.0 at the pH's 8.5, 8.65, 9.0, 9.15, 9.60 and 10.1 respectively. Rate constant also corrected for consecutive reaction (.69) between B and L. **(.69)** A consecutive reaction to (.68) products not determined. Rate constant gives order of magnitude only.

LITERATURE

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EXCHANGE

Sulfonation of aromatic compounds

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.2	$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 1.55	-5	7.5			*	(4)
							40	k_1 1.68	-6					
							40	k_2 4.63	-3					
							40	q 3.89	+3					
.3	$CH_3C_6H_5 + H_2SO_4 \longrightarrow CH_3C_6H_4SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 7.87	-5	6.8			*	(4)
							40	k_1 7.95	-6					
							40	k_2 4.67	-3					
							40	q 9.5	+2					
.4	$NO_2C_6H_5 + H_2SO_4 \longrightarrow m\text{-}NO_2C_6H_4SO_3H + H_2O$	A	B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 2.4	-7	11.1			*	(4)
							40	k_1 2.5	-8					
							40	k_2 1.13	-2					
							40	q 1.53	+3					
		B + SO_3 (1-30%)	A < 0.1 $[SO_3]$			k A$[SO_3]$/B	25	6.3	-5	22			*	(2)

SUPPLEMENT 1956

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.5	$(CH_3)_3N^+C_6H_5 + H_2SO_4 \longrightarrow (CH_3)_3N^+C_6H_4SO_3H + H_2O$ (78% *m*, 22% *o,p*)	$B + SO_3$ (1-30%)	$A < 0.1\ [SO_3]$	% SO_3									*	(2)
				4.1		$k\,A$	25	1.2	-5	16.3	1.1	7		
				11.5			25	2.3	-4	14.9	2.0	7		
				20.1			25	2.1	-3	14.9	1.9	8		
				24.2			25	3.0	-3	15.2	5.3	8		
				33.1			25	3.3	-2					
				(1-30)	$k\,A([SO_3]/B)^{2.4}$									
							25	1.2	-2					
.6	$ClC_6H_5 + H_2SO_4 \longrightarrow ClC_6H_4SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k\,AB$; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
							40	k_0 1.06	-5	8.9				
							40	k_1 1.14	-6					
							40	k_2 8.5	-4					
							40	q 1.05	+3					
.7	$BrC_6H_5 + H_2SO_4 \longrightarrow BrC_6H_4SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k\,AB$; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
							40	k_0 9.5	-6	8.9				
							40	k_1 1.04	-6					
							40	k_2 8.2	-4					
							40	q 1.05	+3					
.8	$4\text{-}BrC_6H_4T + H_2SO_4 \longrightarrow Br\text{-}TC_6H_3SO_3H + H_2O$ (k_H) $\longrightarrow 4\text{-}BrC_6H_4SO_3H + HOT$ (k_T)	$B + SO_3$ (10-12%)				k_H/k_T	0	1.82	0				*	(1)
	Di-substituted Benzene													
.9	$m\text{-}(CH_3)_2C_6H_4 + H_2SO_4 \longrightarrow (CH_3)_2C_6H_5SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k\,AB$; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
							40	k_0 1.17	-4	6.4				
							40	k_1 1.24	-5					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.9		$m\text{-}(CH_3)_2C_6H_4 + H_2SO_4 \longrightarrow (CH_3)_2C_6H_5SO_3H + H_2O$ *(continued)*	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k\,AB;\ k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_2 8.79	-3				*	([4])
								40	q 1.61	+3					
.10	.1	$p\text{-}CH_3C_6H_4NO_2 + H_2SO_4 \longrightarrow$ $1\text{-}CH_3\text{-}2\text{-}SO_3H\text{-}4\text{-}NO_2C_6H_3 + H_2O$	B + M	A = 0.2; M = 0.78	$k\,A/M(M + [HSO_4^-])$			70	6.4	-7				*	([3])
				" 1.05				70	7.8	-7					
				" 1.33				70	8.9	-7					
				" 1.78				70	8.3	-7					
				" 2.24				70	1.08	-6					
				" 1.14				80	2.39	-6					
				" 1.36				80	2.56	-6					
				" 1.78				80	2.78	-6					
				" 2.24				80	3.20	-6					
				" 2.73				80	3.33	-6					
				A = 0.1-0.2; M = 1.4-5.5				96	1.9	-5					
				0.4 1.38				96	1.5	-5	27				
				0.2 2.17	$NaHSO_4$	0.2-1.0		96	2.00	-5					
				" 1.47		0.9-2.6		96	1.66	-5					
				" 1.06		0 -0.9		96	1.84	-5					
				" "		2.0		96	1.66	-5					
				" "		2.8		96	1.58	-5					
			B + SO_3	A = 0.2; $[SO_3]$ = 0.44		$k\,A[SO_3]$		13	2.36	-5					
				" 1.1				13	3.1	-5					
				" 2.2				13	4.0	-5					
				" 0.2-0.8				25	8.4	-5					
				" 1.2				25	9.5	-5					
				" 0.3-1.5				40	4.2	-4	18	2	9		
				A < 0.1 $[SO_3]$	$\%SO_3$ = 4.1		$k\,A$	20	1.0	-4				*	([2])
					7.4			20	2.3	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.10	.1	$p\text{-}CH_3C_6H_4NO_2 + H_2SO_4 \longrightarrow$ *(continued)*	$B + SO_3$	$A < 0.1\ [SO_3]$	$\%SO_3 =$	11.4	$k\,A$	20	4.4	-4				*	(2)
						20.1		20	1.2	-3	19.5	6	10		
						4-20	$k'A([SO_3]/B)^{1.2}$								
								20	3.0	-3					
			$C_6H_5NO_2$	$A = 0.1\text{-}0.5;$ $B = 0.1\text{-}0.3$			$k\,AB;\ k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
								40	k_0 3.3	-6	9.8				
								40	k_1 3.5	-7					
								40	k_2 2.75	-3					
								40	q 1.11	+3					
.11		$p\text{-}CH_3C_6H_4N(CH_3)_3^+ + H_2SO_4 \longrightarrow$ $1\text{-}CH_3\text{-}2\text{-}SO_3H\text{-}4\text{-}(CH_3)_3N^+C_6H_3 + H_2O$	$B + SO_3$	$A < 0.1\ [SO_3]$	$\%SO_3 =$	4.1	$k\,A$	25	5.0	-3	13.2	2.6	7	*	(2)
						11.5		25	9.0	-2					
						4-11	$k'A([SO_3]/B)^{2.2}$								
								25	3.5	0					
.12		$p\text{-}CH_3C_6H_4Cl + H_2SO_4 \longrightarrow CH_3\text{-}ClC_6H_3SO_3H + H_2O$	$C_6H_5NO_2$	$A = 0.1\text{-}0.5;$ $B = 0.1\text{-}0.3$			$k\,AB;\ k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
								40	k_0 1.71	-5	7.4				
								40	k_1 1.85	-6					
								40	k_2 4.59	-3					
								40	q 3.36	+3					
.13		$m\text{-}Cl_2C_6H_4 + H_2SO_4 \longrightarrow Cl_2C_6H_3SO_3H + H_2O$	$C_6H_5NO_2$	$A = 0.1\text{-}0.5;$ $B = 0.1\text{-}0.3$			$k\,AB;\ k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
								40	k_0 6.7	-6	9.5				
								40	k_1 9.2	-7					
								40	k_2 1.99	-3					
								40	q 2.36	+3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.14	$p\text{-}Cl_2C_6H_4 + H_2SO_4 \longrightarrow Cl_2C_6H_3SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 9.8	-7	9.6			*	(4)
							40	k_1 1.06	-7					
							40	k_2 1.71	-3					
							40	q 3.00	+3					
.15	$p\text{-}Br_2C_6H_4 + H_2SO_4 \longrightarrow Br_2C_6H_3SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 1.01	-6	9.7			*	(4)
							40	k_1 1.09	-7					
							40	k_2 7.0	-4					
							40	q 2.21	+3					
	Tri-substituted benzene													
.16	$1,2,4\text{-}Cl_3C_6H_3 + H_2SO_4 \longrightarrow Cl_3C_6H_2SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 7.3	-7	9.9			*	(4)
							40	k_1 7.9	-8					
							40	k_2 7.7	-4					
							40	q 3.62	+3					
	Substituted napthalenes													
.17	$C_{10}H_8 + H_2SO_4 \longrightarrow C_{10}H_7SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$	40	k_0 1.41	-4	6.1			*	(4)
							40	k_1 1.14	-5					
							40	k_2 5.64	-3					
							40	q 1.44	+3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.18	$\alpha\text{-}C_{10}H_7NO_2 + H_2SO_4 \longrightarrow C_{10}H_6SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			k AB; $k = k_1[M + (k_1/k_0)^3]^{-1/3} - k_2M/A(1 + qM)$							*	(4)
							40	k_o 2.61	-5	8.4				
							40	k_1 2.98	-6					
							40	k_2 8.17	-3					
							40	q 3.57	+3					

COMMENTS

Reactions. (.2) (.3) Followed by turbidimetric method for H_2O by (4). Rate dependent upon concentration of water as given by expression for k which holds for first 5 to 7% reaction only, and for $[H_2O]<0.015$. k_0 is measured rate constant for initial rate and the k_1 and k_2 terms are related to the forward and reverse reactions. Simultaneous sulfonation of solvent given by (.4). (.4) Reaction followed by turbidimetric method for H_2O by (4). See (.2) (.3). Reaction using spectrophotometric method in fuming sulfuric observed by (2) to be pseudo first order with respect to A as B in excess. Rate constant found to be proportional to first power of the ratio $[H_2S_2O_7]/[H_2SO_4]$ where $[H_2S_2O_7]$ was taken as equal to the SO_3 added. Rate constant calculated in terms of total $C_6H_5NO_2$ and $C_6H_5NO_2H^+$ rather than true $C_6H_5NO_2$ concentration. Units converted to seconds from original minutes of (2). (.5) Analytical method for A with units converted to seconds from original minutes. First order with respect to A as B in excess. Rate constant found to be proportional to the ratio $[H_2S_2O_7]/[H_2SO_4]$ to the 2.4 power. $[H_2S_2O_7]$ taken as equal to the SO_3 added. Temperature dependence studied from 0 to 40°C. (.6) (.7) Followed by a turbidimetric method for H_2O. Expression for dependence of rate upon H_2O valid for first 5 to 7% reaction and for $[H_2O]<0.015$. Measured rate constant for initial rate is k_0. Terms for forward and reverse reactions involve k_1 and k_2. For simultaneous sulfonation of solvent see (.4). (.8) Comparison of sulfonation at hydrogen and tritium studied in both fuming sulfuric and nitrobenzene as solvent. (.9) Followed by a turbidimetric method for H_2O. Expression for dependence of rate upon H_2O valid for first 5 to 7% reac-

COMMENTS *(continued)*

tion and for $[H_2O]<0.015$. Measured rate constant for initial rate is k_0. Terms for forward and reverse reactions involve k_1 and k_2. For simultaneous sulfonation of solvent see (.4). **(.10)** Integrated rate law of ([3]) gives linear plot up to 80% reaction for individual runs but calculated constants increase with increase in concentration of either H_2O, or SO_3. Activation energy in presence of H_2O can be corrected by 20 kcal. for the heat of reaction of H_2O and SO_3 at infinite dilution in H_2SO_4 to give a value of 7 kcal. The rate law in excess H_2O or SO_3 consistent with mechanism involving simultaneous attack of both a sulfonating agent and a base to remove the proton. Units converted to seconds from original hours of ([3]). Pseudo first order with respect to A observed by ([2]) as SO_3 in larger excess. At these concentrations rate constant observed to be proportional to $[H_2S_2O_7]/[H_2SO_4]$ to the 1.2 power, where $[H_2S_2O_7]$ is taken as amount of SO_3 added. Units converted to seconds from original minutes of ([2]). Turbidimetric method for H_2O in $C_6H_5NO_2$ used by ([4]). Expression for dependence of rate upon H_2O valid for first 5 to 7% reaction, and for $[H_2O]<0.015$. Measured initial rate constant is k_0 and terms for forward and reverse reactions involve k_1 and k_2. For simultaneous sulfonation of solvent see (.4). **(.11)** Pseudo first order with respect to A for at least 60% of reaction as B in excess. Rate found to be proportional to $[H_2S_2O_7]/[H_2SO_4]$ to the 2.2 power. $[H_2S_2O_7]$ taken as equal to the SO_3 added. Addition of a base such as HSO_4^- reduces rate. Units converted to seconds from original minutes. **(.12) (.13) (.14) (.15) (.16) (.17) (.18)** Measured rate constant for initial reaction is k_0. Net forward reaction given by k valid for 5-7% reaction and for $[H_2O]<0.015$. Term involving k_1 is for forward reaction and term involving k_2 is for reverse reaction. For simultaneous sulfonation of solvent see (.4). Turbidimetric method used.

LITERATURE

([1]) U. Berglund-Larsson, L. Melander, *Arkiv. Kemi.* 1953, **6**, 219. ([2]) J.C. Brand, *CSL* 1950, 1004.

([3]) W.A. Cowdrey, D.S. Davies, *CSL* **1949**, 1871. ([4]) F.J. Stubbs, C.D. Williams, C.N. Hinshelwood, *CSL* **1948**, 1065.

EXCHANGE

Aryl sulfone formation

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $ArH + RSO_2X \longrightarrow ArSO_2R + HX$
(A) (B) (L) (M)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E
.1	$C_6H_6 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2C_6H_5 + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	3.5	-5	
.2	$C_6H_6 + p\text{-}CH_3C_6H_4SO_2Cl \longrightarrow p\text{-}C_6H_5SO_2C_6H_4CH_3 + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	1.08	-4	
.3	$C_6H_6 + m\text{-}NO_2C_6H_4SO_2Cl \longrightarrow m\text{-}C_6H_5SO_2C_6H_4NO_2 + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	2.3	-6	
.4	$C_6H_6 + p\text{-}ClC_6H_4SO_2Cl \longrightarrow p\text{-}C_6H_5SO_2C_6H_4Cl + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	1.8	-5	
.5	$C_6H_6 + p\text{-}BrC_6H_4SO_2Cl \longrightarrow p\text{-}C_6H_5SO_2C_6H_4Br + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30 40	1.8 4.5	-5 -5	 17
.6	$C_6H_6 + p\text{-}IC_6H_4SO_2Cl \longrightarrow p\text{-}C_6H_5SO_2C_6H_4I + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	2.3	-5	
.7	$CH_3C_6H_5 + p\text{-}BrC_6H_4SO_2Cl \longrightarrow CH_3C_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.1	$AlCl_3$	0.1	kB	30	6.8	-5	
.8	$NO_2C_6H_5 + p\text{-}BrC_6H_4SO_2Cl \longrightarrow$	A	B = 0.2	$AlCl_3$	0.2	(no measurable reaction)				
.9	$ClC_6H_5 + p\text{-}BrC_6H_4SO_2Cl \longrightarrow ClC_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.2	$AlCl_3$	0.2	kB	30	1.3	-5	
.10	$BrC_6H_5 + p\text{-}BrC_6H_4SO_2Cl \longrightarrow BrC_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.2	$AlCl_3$	0.2	kB	30	1.7	-5	

COMMENTS

Pseudo first order with respect to B as A in excess. Order with respect to catalyst, $AlCl_3$, not determined. Beyond 50% reaction calculated rate constants decrease. Units in seconds calculated from original minutes.

LITERATURE

S. C. J. Olivier, *RTC* 1914, **33**, 146, 244.

EXCHANGE

Replacement of H by halogen on aliphatic C

Reaction type: $RH + X_2 \longrightarrow RX + HX$ (unless otherwise stated)
(A) (B) (L) (M)

Rate measured: $-dB/dt$ unless otherwise stated

Amounts are in M/l. Rates and rate constants are in M/l and sec.

Where there may be doubt about the position of the substitution, the H exchanged is printed in bold-face type.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
		Saturated aliphatic Derivatives													
.44		$C_2H_5(CH_3)_2COH + Br_2 \longrightarrow$	CCl_4	A = 0.046	M	0-0.05	k B	25	3.8	-6				*	([1])
		$CH_3CHBr(CH_3)_2CBr + H_2O$		0.095				25	1.20	-5					
				0.191				25	4.6	-5					
				0.381				25	1.70	-4					
				0.762				25	4.3	-4					
				1.52 (B = 0.008-0.2)				25	9.4	-4					
				4.57				25	4.95	-3					
.45		$(CH_3)_3CBr + Br_2$	CCl_4	A = B = 1.0	$[(CH_3)_3CO]_2$	0-2%	k AB^2	0	1.44	-6				*	([27])
		Aliphatic-aliphatic mono Ketone													
.46	.1	$CH_3COCH_3 + 3ClO^- \longrightarrow$	H_2O	A = 0.31;	OH^-	0.034	k AB	0	1.02	-3				*	([2])
		$CH_3COO^- + CHCl_3 + 2OH^-$		10^3B = 1.5		0.071		0	1.53	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.46	.1	$CH_3COCH_3 + 3ClO^- \longrightarrow$ *(cont.)*	H_2O	A = 0.31; 10^3B = 1.5	OH^- Cl^-	0.034 0.22	k AB	0	1.24	-3				*	([2])
.47	.2	$CH_3COCH_3 + Br_2$	H_2O	A = 0.1; B = 0.005	HCl	0.5	k A	5	1.27	-6				*	([11])
								15	4.61	-6					
								25	1.53	-5					
								35	5.16	-5	20.3				
			Ac25	"	"	"	"	15	5.72	-6					
								25	1.85	-5					
								35	5.76	-5	20.0				
			Ac50	"	"	"	"	0	1.14	-6					
								15	7.68	-6					
								25	2.49	-5	19.7				
			Ac75	"	"	"	"	0	2.26	-6					
								15	1.63	-5					
								25	5.27	-5	20.1				
			H_2O	A = 0.1; B = 0.005	CH_3COO^-	0.147	k A	35	8.91	-7				*	([11])
								45	2.58	-6					
								55	7.05	-6	20.7				
			Ac25	"	"	"	"	35	1.54	-6					
								45	4.32	-6					
								55	1.12	-5	19.0				
			Ac50	"	"	"	"	35	2.36	-6					
								45	6.40	-6					
								55	1.68	-5	19.4				
			Ac75	"	"	"	"	35	2.92	-6					
								45	7.66	-6					
								55	1.88	-5	18.5				

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.47	.2	$CH_3COCH_3 + Br_2$ *(cont.)*	Ac90	A = 0.1; B = 0.005	CH_3COO^-	0.147	k A	35	2.82	-6				*	(11)
								45	7.50	-6					
								54	1.97	-5	19.3				
.48	.2	$CH_3COCH_3 + 3BrO^- \longrightarrow CH_3COO^- + CHBr_3 + 2OH^-$	H_2O	10^4A = 7-8; 10^3B = 1.5-5	OH^-	0.007-0.07	$k\,A[OH^-]$	0	6.7	-2				*	(2) (7)
								10	1.60	-1					(7)
								18	3.12	-1					
								25	5.2	-1	13.4	3.5	9		
.49	.4	$CH_3COCH_3 + I_2$	H_2O	A = 0.27; 10^3B = 1-2	(X_1)	buffers	$\Sigma k_1 AX_1$							*	(6)
					H_2O	55.5	k_1	25	8	-12					
					OH^-		k_1	25	2.5	-1					
					H_3O^+		k_1	25	2.74	-5					
					$(CH_3)_3CCOO^-$	$(5-20)\ 10^{-3}$	k_1	25	4.08	-7					
					$(CH_3)_3CCOOH$	$(2-20)\ 10^{-3}$	k_1	25	7.3	-8					
					CH_3COO^-	$(2-10)\ 10^{-3}$	k_1	25	2.44	-7					
					CH_3COOH	$(4-100)\ 10^{-4}$	k_1	25	1.01	-7					
					CH_2OHCOO^-	μ = 0.11	k_1	25	3.85	-8					
					$CH_2OHCOOH$	μ = 0.11	k_1	25	3.25	-7					
					CH_2ClCOO^-	μ = 0.2	k_1	25	5.0	-9					
					$CH_2ClCOOH$	μ = 0.2	k_1	25	1.27	-6					
					$C_6H_2Cl_3O^-$	μ = 0.11	k_1	25	7.56	-6					
			H_2O	A = 0.27; 10^3B = 2	CH_3COO^-	0.02-0.2	(see comments)							*	(5) (28)
					CH_3COOH	0.02-0.8									
						μ = 0.2									
.50	.4	$CH_3COCH_3 + 3IO^- \longrightarrow CH_3COO^- + CHI_3 + 2OH^-$	H_2O	10^4A = 7-8; 10^3B = 1.5-5	OH^-	0.007-0.035	$k\,A[OH^-]$	0	6.9	-2				*	(2) (7)
								10	1.60	-1					(7)
								18	3.12	-1					
								25	5.2	-1	13.4	3.5	9		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.51		$CH_3COCH_3 + 2,4\text{-}Cl_2C_6H_4N(C{:}OCH_3)Cl \longrightarrow CH_3COCH_2Cl + 2,4\text{-}Cl_2C_6H_4NHCOCH_3$	C_6H_5Cl	$10^2B = 0.85$	$CH_2ClCOOH$	0.0138	$-dB^o/dt$	50	7.85	-8				*	(6)
				1.5		0.0138		50	8.65	-8					
				3.0		0.0138		50	1.73	-7					
				6.2		0.0138		50	3.08	-7					
				A = 1.23 9.5		0.0138		50	3.17	-7					
				15.7		0.0138		50	4.14	-7					
				2.2		0.0072		50	9.84	-8					
				5.0		0.0072		50	1.69	-7					
				7.6		0.0072		50	2.06	-7					
				15.1		0.0072		50	2.40	-7					
.52		$CH_3COCH_3 + [(2,4,6\text{-}Cl_3C_6H_2)ClN]_2C{:}O \longrightarrow CH_3COCH_2Cl + [(2,4,6\text{-}Cl_3C_6H_2)HN]_2C{:}O$	C_6H_5Cl	$10^2B = 3.4$	$CH_2ClCOOH$	0.0072	$-dB^o/dt$	50	2.11	-7				*	(6)
				5.5		0.0072		50	2.60	-7					
				A = 1.23 10.5		0.0072		50	3.17	-7					
				17.6		0.0072		50	3.25	-7					
.53		$CH_3CH_2COCH_2CH_3 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15	1.55	-5				*	(17)
								25	5.42	-5					
								35	1.72	-4	21.2	2.0	11		
.54		$(CH_3)_3CCOCH_3 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	2.34	-5				*	(17)
								35	7.40	-5					
								45	2.02	-4	20.3	1.8	10		
.55		$C_2H_5CH_2COCH_2C_2H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15	1.36	-5				*	(17)
								25	4.41	-5					
								35	1.42	-4	20.6	6	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.56		$(CH_3)_2CHCOCH(CH_3)_2 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	35	2.02	-5				*	(17)
								45	6.65	-5					
								55	1.99	-4	22.8	3	11		
.57		$(CH_3)_3CCOCH_2CH_3 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	9.0	-6				*	(17)
								35	2.90	-5					
								45	9.4	-5	21.8	9	10		
.58		$(CH_3)_3CCOCH_2C_2H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	8.0	-6				*	(17)
								35	2.56	-5					
								45	8.0	-5	21.3	3	10		
.59		$(CH_3)_3CCOCH(CH_3)_2 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	35	1.74	-6				*	(17)
								45	5.98	-6					
								55	1.72	-5	22.7	2	10		
		Halogen-substituted Ketones													
.60		$CH_3COCH_2Cl + I_2$	H_2O	$10^2A = 2\text{-}6$	buffers	$\mu = 0.11$	$\Sigma k_i AX_i$							*	(6)
					X = H_2O	"	k_i =	25	4.8	-9					
					OH^-	"	k_i =	25	2.0	+2					
					H_3O^+	"	k_i =	25	< 3	-6					
					$(CH_3)_3CCOO^-$	"	k_i =	25	2.64	-4					
					CH_3COO^-	"	k_i =	25	1.87	-4					
					CH_2OHCOO^-	"	k_i =	25	2.52	-5					
					CH_2ClCOO^-	$\mu = 0.2$	k_i =	25	4.59	-6					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.61		$CH_3COCH_2Br + I_2$	H_2O		buffers		$\sum k_1 AX_1$							*	(6)
					$X_1 = H_2O$	$\mu = 0.11$	$k_1 =$	25	9.7	-9					
					OH^-	"	$k_1 =$	25	9.3	+2					
					H_3O^+	"	$k_1 =$	25	6.32	-5					
					$(CH_3)_3CCOO^-$	"	$k_1 =$	25	1.85	-4					
					CH_3COO^-	"	$k_1 =$	25	1.07	-4					
					CH_2OHCOO^-	"	$k_1 =$	25	1.75	-5					
					CH_2ClCOO^-	$\mu = 0.2$	$k_1 =$	25	2.97	-6					
					$C_6H_2Cl_3O^-$	$\mu = 0.11$	$k_1 =$	25	5.30	-3					
.62		$CH_3COCHCl_2 + Br_2$	H_2O		buffers	$\mu = 0.11$	$\sum k_1 AX_1$							*	(6)
					$X_1 = H_2O$	"	$k_1 =$	25	1.32	-8					
					OH^-	"	$k_1 =$	25	4.5	+2					
					H_3O^+	"	$k_1 =$	25	1.8	-7					
					$(CH_3)_3CCOO^-$	"	$k_1 =$	25	1.34	-3					
					CH_3COO^-	"	$k_1 =$	25	5.63	-4					
					CH_2ClCOO^-	$\mu = 0.2$	$k_1 =$	25	2.08	-5					
		Keto-Ketones													
.63		$CH_3COCH_2CH_2COCH_3 + I_2$	H_2O		buffers		$\sum k_1 AX_1$							*	(6)
					H_2O	$\mu = 0.11$	$k_1 =$	25	4.2	-11					
					OH^-	"	$k_1 =$	25	1.7	0					
					H_3O^+	"	$k_1 =$	25	2.52	-5					
					$(CH_3)_3CCOO^-$	"	$k_1 =$	25	2.52	-6					
					CH_3COO^-	"	$k_1 =$	25	1.43	-6					
					CH_2OHCOO^-	"	$k_1 =$	25	2.94	-7					
					CH_2ClCOO^-	$\mu = 0.2$	$k_1 =$	25	2.5	-8					
					CH_3COOH	$\mu = 0.11$	$k_1 =$	25	6.3	-8					
					$CH_2OHCOOH$	"	$k_1 =$	25	2.2	-7					
					$CH_2ClCOOH$	$\mu = 0.2$	$k_1 =$	25	9.7	-7					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.64		$CH_3COCH(CH_3)COCH_3 + Br_2$	H_2O	$10^2A = 3.3$;			kA	21	5.8	-5					(21)
				$10^3B = 3$				25	8.3	-5					
								35	2.3	-4	18	1.2	9		
.65		$CH_3COCH_2COCF_3 + Br_2$	H_2O	$10^2A = 4\text{-}8$;	HCl	0	kA	0	8.99	-4				*	(26)
				$10^2B = 4\text{-}8$		0		14	4.65	-3					
						0-0.1		25	1.48	-2	19.7	4.1	13		
						0.5		25	1.57	-2					
			Et16			0		25	1.49	-2					
			Et33			"		25	1.37	-2					
			Et50			"		25	1.37	-2					
			Et67			"		25	1.26	-2					
			Et83			"		25	9.27	-3					
			Et95			"		25	6.44	-3					
.66		$(CH_3)_2CHCH_2COCH_2COCF_3 + Br_2$	Et6	$A \simeq B \simeq 0.015$			kA	14	3.42	-3				*	(26)
								25	1.18	-2	19	1	12		
.67		$C_6H_5COCH_2COCF_3 + Br_2$	Et4	$A \simeq B \simeq 0.01$			kA	14	3.72	-3				*	(26)
								25	8.55	-3	13	3	7		
.68		CH-CH ‖ ‖ CH CHCOCH$_2$COCF$_3$ + Br_2 \S/	Et10	$A \simeq B \simeq 0.01$			kA	14	2.96	-3				*	(26)
								25	1.01	-2	19	8	11		
Aromatic-aliphatic Ketone															
.69	.13	$CH_3COC_6H_5 + Br_2$	Ac25	A=0.1; B=0.005	HCl	0.5	kA	25	7.12	-6				*	(11)
								35	2.13	-5					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.69	.13	$CH_3COC_6H_5 + Br_2$ *(cont.)*	Ac25	A = 0.1; B = 0.005	HCl	0.5	*k* A	45	5.77	-5	19.4			*	(11)
			Ac50	" "	"	"	"	25	9.16	-6					"
								35	2.70	-5					
								45	7.34	-5	19.2				
			Ac75	" "	"	"	"	15	6.25	-6					(11) (15) (16)
								25	2.03	-5					
								35	6.28	-5					
								45	1.81	-4	20.2	1.3	10		
			Ac90	" "	"	"	"	5	1.05	-5					(11)
								15	3.72	-5					
								25	1.20	-4	19.8				
			Ac50	" "	CH_3COO^-	0.147	*k* A	35	1.28	-6				*	(11)
								45	3.58	-6					
								55	9.91	-6	20.3				
			Ac75	" "	"	"	"	35	1.28	-6					"
								45	4.0	-6					(11) (15)
								55	1.01	-5					
								65	2.75	-5	18.9	4	7		(15)
			Ac90	" "	"	"	"	35	1.31	-6					
								45	3.52	-6					
								55	9.25	-6	19.3				
.70	.14	$CH_3CO(m\text{-}C_6H_4CH_3) + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	*k* A	15	7.43	-6				*	(16)
								25	2.47	-5					
								35	7.41	-5	20.0	1.2	10		
.71	.15	$CH_3CO(m\text{-}C_6H_4NO_2) + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	*k* A	15	2.5	-6				*	(16)
								25	8.2	-6					
								35	2.70	-5					
								45	7.96	-5	21.0	2.1	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.72	.16	$CH_3CO(p\text{-}C_6H_4NO_2) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	15	3.16	-6				*	([16])
								25	9.8	-6					
								35	3.16	-5					
								45	9.5	-5	21.0	2.5	10		
.73	.17	$CH_3CO(m\text{-}C_6H_4F) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	25	1.38	-5				*	([16])
								35	4.36	-5					
								45	1.28	-4	20.7	2.1	10		
.74	.18	$CH_3CO(p\text{-}C_6H_4F) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	25	1.49	-5				*	([16])
								35	4.78	-5					
								45	1.36	-4	20.5	1.7	10		
.75	.19	$CH_3CO(m\text{-}C_6H_4Cl) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	15	3.58	-6				*	([16])
								25	1.22	-5					
								35	3.92	-5					
								45	1.15	-4	20.8	2.2	10		
.76		$CH_3CO(p\text{-}C_6H_4Cl) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	15	4.7	-6				*	([16])
								25	1.52	-5					
								35	4.73	-5					
								45	1.40	-4	20.6	2.0	10		
.77	.20	$CH_3CO(m\text{-}C_6H_4Br) + Br_2$	Ac75	A=0.1; B=0.005	HCl	0.5	k A	15	3.63	-6				*	([16])
								25	1.23	-5					
								35	3.99	-5					
								45	1.17	-4	20.8	2.2	10		

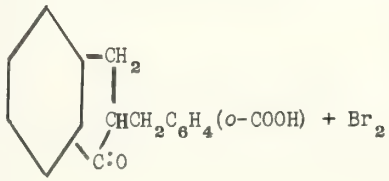
No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.78	.21	$CH_3CO(p\text{-}C_6H_4Br) + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15	4.83	-6				*	([16])
								25	1.54	-5					
								35	4.74	-5					
								45	1.45	-4	20.4	1.4	10		
.79	.22	$CH_3CO(m\text{-}C_6H_4I) + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15	3.71	-6				*	([16])
								25	1.25	-5					
								35	4.03	-5					
								45	1.17	-4	20.7	1.9	10		
.80	.23	$CH_3CO(p\text{-}C_6H_4I) + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	1.62	-5				*	([16])
								35	4.97	-5					
								45	1.47	-4	20.4	1.5	10		
.81	.28	$CH_3CH_2COC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	9.0	-6				*	([14])
								35	2.94	-5					
								45	9.35	-5	22.1	1.4	11		
			"	" "	CH_3COO^-	0.147	k A	45	6.65	-7				*	([15])
								55	1.81	-6					
								65	4.72	-6	19.9	3	7		
.82	.30	$C_2H_5CH_2COC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	6.01	-6				*	([14])
								35	2.03	-5					
								45	6.45	-5	22.0	8	10		
			"	" "	CH_3COO^-	0.147	k A	45	5.20	-7				*	([15])
								55	1.43	-6					
								65	3.62	-6	20.2	4	7		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.83	.32	$(CH_3)_2CHCOC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	1.77	-6				*	(14)
								35	6.06	-6					
								45	1.92	-5	22.1	2.9	10		
			"	" "	CH_3COO^-	0.147	k A	45	1.27	-7				*	(15)
								55	3.70	-7					
								65	9.9	-7	20.9	3	7		
.84	.34	$n\text{-}C_3H_7CH_2COC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	7.10	-6				*	(14)
								35	2.36	-5					
								45	7.30	-5	21.7	6	10		
			"	" "	CH_3COO^-	0.147	k A	45	5.86	-7					(15)
								55	1.57	-6					
								65	3.99	-6	20.1	4	7		
.85	.35	$(CH_3)_2CHCH_2COC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	2.79	-6				*	(15)
								35	9.34	-6					
								45	2.89	-5	21.7	2.3	10		
			"	" "	CH_3COO^-	0.147	k A	45	2.54	-7					
								55	7.07	-7					
								65	1.87	-6	20.5	3.2	7		
.86	.36	$n\text{-}C_4H_9CH_2COC_6H_5 + Br_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25	6.81	-6				*	(14)
								35	2.22	-5					
								45	6.86	-5	21.4	3.4	10		
		Mono-carboxylic acids													
.87		$CH_3COONa + Br_2$	CH_3COOH	A = 2B = 0.025	NaBr	0.65	k AB	25	1.58	-2				*	(13)
						"		35	3.18	-2	16		~11		
			Ac92			0.2		35	6.0	-2					
			Ac80			0.2		35	1.4	-1					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.88		$CH_3COONa + I_2$	CH_3COOH	A = 0.01; B = 0.2			k AB	25	6.6	-5				*	(12)
								35	2.34	-4	25				
Keto-carboxylate															
.89	.10	$CH_3COCH_2COOC_2H_5 + Br_2$	H_2O	10^3A = 5-17	KBr	0.05	k A	0	1.35	-4				*	(23)
						"		18	6.85	-4					
						"		25	1.20	-3					
					NaCl	0.10		18	6.85	-4					
						0.30		18	6.65	-4					
						0.60		18	6.26	-4					
						1.00		18	5.69	-4					
						2.00		18	4.35	-4					
					HCl	0.0		18	6.92	-4					
						0.042		18	7.08	-4					
						0.099		18	7.19	-4					
						0.20		18	7.30	-4					
						0.37		18	7.54	-4				*	
			"	10^3A = 4-8; B < A	Cu^{++}	0-0.02	$k A + k' A[Cu^{++}] + k'' A[CH_3COO^-] + k''' A[Cu^{++}][CH_3COO^-]$								(24)
					CH_3COONa	0.010		18	k = 7.12	-4					
					CH_3COOH	0.10		18	k' = 1.03	-1					
								18	k'' = 3.15	-1					
								18	k''' = 4.4	+1					
.90		$CH_3COCHBrCOOC_2H_5 + Br_2$	H_2O	$10^3A \sim 5$	KBr	0.05	k A	0	1.59	-3				*	(23)
						"		18	8.30	-3					
						"		25	1.47	-2					
					NaCl	0.10		18	8.26	-3					
						0.30		18	7.50	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.90		$CH_3COCHBrCOOC_2H_5 + Br_2$ *(cont.)*	H_2O	$10^3A \sim 5$	NaCl	0.60	kA	18	6.92	-3				*	(23)
						1.00		18	6.45	-3					
						2.00		18	5.65	-3					
					HCl	0.0		18	7.92	-3					
						0.04-0.1		18	7.19	-3					
						0.20		18	7.35	-3					
						0.37		18	7.54	-3					
					Cu^{++}	0-0.02		18	8.0	-3				*	(24)
.91		$CH_3COCH(C_2H_5)COOC_2H_5 + Br_2$	H_2O	A= 0.03; B= 0.001			kA	20	4.8	-6					(21)
								25	7.6	-6					
								35	1.73	-5	15.5	1.6	6		
.92		$CH_2CH_2CH_2C{:}OCHCOOC_2H_5 + Br_2$	H_2O	$10^3A = 3\text{-}7$; $B < A$	Acids + salts	0-0.1	$kA + \sum k_i AX_i$							*	(25)
						0-0.3		18	k = 1.34	-3					
					$X_i = Cu^{++}$			18	k_i = 1.22	-1					
					Ni^{++}			18	k_i = 8.25	-2					
					La^{+++}			18	k_i = 5.65	-2					
					Zn^{++}			18	k_i = 2.11	-2					
					Pb^{++}			18	k_i = 1.07	-2					
					Mn^{++}			18	k_i = 6.5	-3					
					Cd^{++}			18	k_i = 6	-3					
					Mg^{++}			18	k_i = 4.3	-3					
					Ca^{++}			18	k_i = 4.1	-3					
					Ba^{++}			18	k_i = 1.1	-3					
					H^+			18	k_i = 7.1	-4					
					Be^{++}			18	k_i = 5	-4					
					Al^{+++}			18	$k_i \sim 4$	-4					
					Na^+			18	k_i = 5	-5					
					K^+			18	k_i = (0.0)						

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
92		$CH_2CH_2CH_2C{:}OCHCOOC_2H_5 + Br_2$	H_2O	$10^3A = 3\text{-}7$; $B < A$	Acids +	0-0.1	$kA + \Sigma k_1AX_1$							*	(25)
					salts	0-0.3									
		(cont.)			$X_1 = Co(NH_3)_4^{+++}$			18	$k_1 = -4$	-4					
					Cl^-			18	$k_1 = -2.9$	-4					
					NO_3^-			18	$k_1 = -4.5$	-4					
					Br^-			18	$k_1 = -8$	-4					
					ClO_4^-			18	$k_1 = -9.0$	-4					
				$10^3A = 2$; $10^4B = 1$	H^+	0.0009-0.07	kA	25	2.30	-3					(8)
					buffers	$\mu = 0.1$	$kA + \Sigma k_1AX_1$								
					$X_1 = (CH_3)_3CCOO^-$			25	$k_1 = 1.02$	0					
					CH_3COO^-			25	$k_1 = 7.0$	-1					
					CH_2OHCOO^-			25	$k_1 = 1.96$	-1					
					CH_2ClCOO^-			25	$k_1 = 5.7$	-2					
					$H_2PO_4^-$			25	$k_1 = 5.1$	-2					
				$10^3A = 4$; $B < A$	$X = Cu^{++}$	0.005-0.01	$kA + k'AX + k''A[CH_3COO^-] + k'''A[CH_3COO^-]X$							*	(24)
					CH_3COO^-	0.006-0.01		18	$k = 1.33$	-3					
					CH_3COOH	0.01-0.1		18	$k' = 1.22$	-1					
								18	$k'' = 4.09$	-1					
								18	$k''' = 1.14$	+2					
					$X = Ni^{++}$										
					CH_3COO^-			18	$k' = 8.25$	0					
					CH_3COOH			18	$k''' = 6.0$	+1					
93		$CH_2CH_2CH_2CH_2C{:}OCHCOOC_2H_5 + I_2$	H_2O	$10^3A = 1\text{-}3$	HCl	$(4\text{-}7) \times 10^{-6}$	kA	25	9.7	-6				*	(4)
				$10^4B = 2\text{-}7$	buffers	$\mu = 0.1$	$kA + \Sigma k_1AX_1$								
					$X_1 = (CH_3)_3CCOO^-$			25	8.29	-3					
					CH_3COO^-			25	5.35	-3					
					CH_2OHCOO^-			25	1.28	-3					
					CH_2ClCOO^-			25	3.0	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.94		 $CHCH_2C_6H_4(o\text{-}COOH) + Br_2$ (2-o-carboxybenzlindan-1-one)	Ac90 (16 M/l)	10^2B = 4.2; 6.8; 2-6; 3-5 ($A = 0.05$)	HBr	0.245; 0.245; 0.303; 0.352	k A	25; 25; 25; 25	2.77; 2.93; 3.85; 5.36	-4; -4; -4; -4					(18)
Dicarboxylic acid (ester)															
.95		$H_2C(COOC_2H_5)_2 + 2Br_2$	H_2O	10^3A = 5-25; 10^3B = 1-3		$-dA/dt = k$ A		25	3.0	-5				*	(3) (21)
.95.1		$H_2C(COOC_2H_5)_2 + Br_2$	H_2O	10^4A = 4-70; 10^4B = 2-200	$HClO_4$	$(2\text{-}8\,10) \times 10^{-5}$	k A	25	2.38	-5				*	(9)
				$10^4[H]^+$ = 8.4-25	CH_2ClCOO^-	0.050		25	6.0	-5					
				" 81		0.028		25	4.37	-5					
				" 25		0.022		25	3.95	-5					
				$10^5[H^+]$ = 3-19	CH_3COO^-	0.020		25	4.93	-4					
.96		$BrHC(COOC_2H_5)_2 + Br_2$	H_2O	$10^4A \sim 4$; $10^2B = 2$	$HClO_4$	0.0011	k A	25	2.6	-4				*	(9) (21)
					CH_2ClCOO^-, $CH_2ClCOOH$	0.05, 0.05		25	6.2	-4					
					CH_3COO^-, CH_3COOH	0.002, 0.002		25	6.0	-4					
					X = CH_2ClCOO^-		k AX	25	6.9	-3					
					CH_3COO			25	1.7	-1					

Supplement 1955

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.97		$C_2H_5CH(COOC_2H_5)_2 + Br_2$	H_2O	$10^2A \sim 3$; $10^3B \sim 3$			k A	25	3	-7				*	(21)
		Nitriles													
.98		$CH_2(CN)_2 + 2Br_2$	H_2O	10^3A = 2-3;			$-dA/dt = k$ A	0	1.00	-3				*	(20)
				10^3B = 6-23				10	2.9	-3	18	2	11		
				10^3B = 2.5	HBr	0.0014		0	6.0	-4					
				$10^3A \sim 1$ 11.8		0.0089		0	5.6	-4					
				2.5		0.0027		0	3.4	-4					
				5.9		0.0089		0	3.2	-4					
.99		$CHBr(CN)_2 + Br_2$	H_2O				k A	0	> 2	-1				*	(20)
.100		$C_2H_5OC{:}OCH_2CN + Br_2$	H_2O	B >> A			$-dA/dt = k$ A	0	7.1	-5				*	(20)
								10	2.3	-4	17	2	9		
.101		$C_2H_5OC{:}OCHBrCN + Br_2$	H_2O					0	8	-2				*	(20)
		Nitro-compounds													
.102		$CH_3CH_2NO_2 + Br_2$	H_2O	A = 0.3-0.4;			k A	26	4.1	-8				*	(19)
				B = 0.02				35	1.23	-7	23	1	9		
.103		$CH_3CH_2NO_2 + I_2$	H_2O	A = 0.3-0.4;			k A	15	9.1	-9				*	(19)
				10^3B = 2-7				26	4.0	-8					
					(X)			35	1.27	-7	22.9	1.2	9		
			"	A = 0.1-0.2;	C_5H_5N	= A	k AX	17	6.07	-5				*	(22)
				10^3B = 2-4				25	1.49	-4					
								35	3.57	-4	16.6	$\Delta S^{\ddagger} = -25$			

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.103		$CH_3CH_2NO_2 + I_2$ *(cont.)*	Et30	A = 0.1-0.2; 10^3B = 2-4	(X) C_5H_5N	= A	k AX	0	8.61	-6				*	(22)
								25	1.08	-4					
								35	2.32	-4	15.8	$\Delta S^{\ddagger}$ = -28			
			Et70	"	"	"	k AX	0	4.6	-7					
								25	5.87	-6					
								35	1.62	-5	17.1	$\Delta S^{\ddagger}$ = -30			
			Et30	"	2-$CH_3C_5H_4N$ = A		k AX	25	4.1	-4					
					3-$CH_3C_5H_4N$ "			25	2.20	-4					
					4-$CH_3C_5H_4N$ "			25	3.03	-4					
					2,6-$(CH_3)_2C_5H_3N$ = A			25	3.47	-4					
					C_9H_7N "			25	7.5	-5					
					iso-C_9H_7N "			25	1.27	-4					
					2-$CH_3C_9H_6N$ "			25	1.28	-4					
.104		$CH_3COCH_2NO_2 + 2Br_2$	H_2O				$-dA/dt = kA$	0	2.0	-3				*	(20)
								10	6.4	-3	19	3	12		
.105		$C_2H_5OC{:}OCH_2NO_2 + 2Br_2$	H_2O				$-dA/dt = kA$	0	5.3	-4				*	(20)
								10	1.52	-3	16	3	9		
.106		$CH_2(NO_2)_2 + 2Br_2$	H_2O				$-dA/dt = kA$	0	4.5	-2				*	(20)
.107		$CH_3CHClNO_2 + Br_2$	H_2O	A > B; A < B			kA	35	1.7	-6				*	(20)
								48	6.2	-6	20	3	8		

SOLVENTS

Ac25 (50, 75, 80, 90, 92) vol of $CH_3COOH + H_2O$ to make 100 volumes.

Et4 (6, 10, 16, 30, 33, 50, 67, 70, 83, 95) $H_2O + C_2H_5OH$ vol %

COMMENTS

General. See comments 1951 edition. For ketones and keto-acids rate determining step considered to be enolization and or ionization of C-H bond. The rates and rate constants listed are for rate of disappearance of halogen, unless otherwise specified. Since replacement of first hydrogen by halogen is generally slower than replacement of second or third hydrogen on the same carbon the measured rate of disappearance of halogen may be two or even three times that of the rate controlling enolization or ionization. Since organic compound usually is in excess of halogen measured rates are pseudo zero order, and first order rate constants are obtained by dividing pseudo zero order rate of disappearance of halogen by concentration of compound being halogenated.

Literature. ([1]) ([2]) ([3]) ([4]) ([5]) ([6]) ([7]) ([8]) ([9]) converted from original minutes. ([11]) ([14]) ([15]) ([16]) ([17]) converted from original minutes and from ml. of N/50 thiosulfate per 20 ml. ([18]) ([19]) ([20]) ([21]) ([22]) ([23]) ([24]) ([25]) converted from original minutes. ([27]) converted from original hours.

Reactions. **(.44)** Pseudo first order with respect to B over about 65% of reaction as A in sufficient excess. At the higher concentrations of A reaction approximately first order with respect to A as k/A almost constant. At lower concentrations reaction more nearly second order with respect to A and k/A^2 almost constant. Authors suggest mechanism involving an intermediate A·B complex consistent with data. Decomposition of complex found to be first order and rate law determined. **(.45)** Rate law not confirmed, except that it is an over-all third order, as A = B in all cases. Addition of *t*-butyl-peroxide reduces rate about 25%. **(.46)** Rate controlling step considered to involve reaction of OCl^- with enol or enolate ion rather than rate of formation of enol and enolate ion. Hydroxyl ion effect attributed to shift of enolate ion equilibrium as doubling OH^- increases rate by only 50%. **(.47)** First order constants calculated from pseudo zero order rates corrected from 1951 edition in which rates were in equivalents of halogen per liter rather than M/l as stated. **(.48)** Rate of enolization, considered to be rate controlling step, would be one third calculated rate as second and third hydrogen replaced more rapidly. **(.49)** Data may be represented by sum of second and third order terms with respective catalytic constants or in terms of concerted termolecular mechanism of ([28]). **(.50)** Rate of enolization, considered to be rate controlling step,

COMMENTS *(cont.)*

would be one third calculated rate as second and third hydrogen replaced more rapidly. **(.51) (.52)** Consecutive mechanism involving reversible enolization followed by reaction with N-halide consistent with data. Rates are expressed in equivalents of oxidizing power of N-halide per liter. **(.60) (.61) (.62) (.63)** Acidity nearly constant in buffered solutions but where change occurred rate constants calculated for average acidity. **(.65) (.66) (.67) (.68)** First order rate law observed up to 80% reaction for all concentrations of A and B studied. Replacement of second hydrogen apparently much slower than first. Longer time intervals however did lead to more than 100% absorption of bromine on basis of amount of A present. **(.69) (.70) (.71) (.72) (.73) (.74) (.75) (.76) (.77) (.78) (.79) (.80) (.81) (.82) (.83) (.84) (.85) (.86)** First order rate constants calculated from pseudo zero order data in terms of ml of N/50 thiosulfate per 20 ml. Corrected from 1951 edition which has rates in equivalents of halogen per liter instead of M/l as listed. **(.87)** Induction period observed. Reaction accelerated (up to a maximum) with H_2O. With different alkali acetates rates are found to vary in the order K > Na > Li. No measurable reaction in pure H_2O. **(.88)** Reaction inhibited by I^-. With different alkali acetates the rate varies in the order K > Na > Li. **(.89) (.90)** Reactions occur consecutively and rate constants calculated for each by analysis of composite data of both reactions. **(.92)** For calculation of catalytic effect of ions K^+ arbitrarily taken as reference ion with $k_x = 0.00$. Where complexing occurs as with Cd^{++} with Br^- simple summation equation is not valid. Catalytic constant for Ni^{++} in CH_3COO^- buffers based upon no complex formation. Assumed complex formation increases value. Variation of concentration of H^+, Cu^{++} and Ni^{++} with time complicates analysis of rates which also vary with time and results of ([25]) are extrapolated to $t = \infty$. No appreciable acid catalysis observed by ([8]). **(.93)** Reaction reversible but measured under conditions leading to almost complete reaction. **(.95)** Composite reaction consisting of consecutive steps (.95.1) and (.96). Rate constants calculated by ([3]) low as the second step, (.96), assumed extremely rapid. **(.95.1)** Replacement of first hydrogen followed by consecutive reaction involving second hydrogen (.96). **(.96)** Value calculated by ([21]) low probably due to error in assumed concentration of A. **(.97)** Decrease in rate with progress of reaction attributed

COMMENTS *(continued)*

to acid hydrolysis of ester occurring simultaneously. **(.98)** Rate determining step probably ionization with ionization of monohalogenated nitrile more rapid than first step. Dependence of rate upon concentration of Br_2 and HBr may be related to a lower reactivity for Br_3^-. **(.99)** Reaction measured in presence of $CH_2(CN)_2$, see (.98) and only one determination. **(.100) (.101)** Consecutive reactions with (.101) determined in presence of some $C_2H_5OCOCH_2CN$ and only one determination. **(.102) (.103)** Assumed to proceed through rate determining ionization. One drop of strong acid added to minimize competition by OH^-. In presence of RN reaction assumed to proceed through slow bimolecular ionization, $RN + CH_3CH_2NO_2 \longrightarrow RNH^+ + CH_3CHNO_2^-$, as rate controlling step followed by rapid reaction between I_2 and the carbanion. **(.104) (.105) (.106) (.107)** Rate determining step assumed to be ionization.

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EXCHANGE

Replacement of H by halogen on aromatic C

Liquid phase

Reaction types: $ArH + X_2 \longrightarrow ArX + HX$

$ArH + HOX \longrightarrow ArX + H_2O$

$ArH + XY \longrightarrow ArX + HY$

Note: For compounds involving more than one aromatic ring, it is understood that substitution takes place in the ring written last. The position of the substituent halogen atom in the product, if given, is designated by a position number counted from the substituent designated in the initial reactant by the number 1.

Amounts are in M/l. Rate constants are in M/l and sec.

* Coded solvents, Comments, Literature at the end of the table.

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Unsubstituted aromatic hydrocarbons															
.272	.2	$C_6H_6 + Br_2$	Ac*	A = 0.095	$ZnCl_2$	0.50	k AB	25	2.2	-4				*	(1)
.272.1	.3	$C_6H_6 + HOBr$	Di 50*	10^2A = 1-1.6; 10^4B = 9-13	$HClO_4$	0.03-0.14	k AB[H^+]	25	5.98	-1					(14b)
.272.2		$C_6H_6 + ICl$	Ac 99*	A = 0.2; 10^3B = 3-7	$ZnCl_2$	1.40	k AB[$ZnCl_2$]	25	<1.6	-7					(26a)
.273		$C_{10}H_8 + Br_2$	Ac 50*	10^3A = 8-16; 10^4B = 8-90	KBr KBr	0.20 0.1-0.5 0.4-0.0 μ = 0.5	k AB $k = k'K_1/(K_1 + [Br^-])$	25	1.91 k' 3.41 K_1 1.64	-2 -1 -2				*	(4a)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.273		$C_{10}H_8 + Br_2$ *(continued)*	Ac 50*	10^3A = 8-16; 10^4B = 8-90	KBr, NaClO	0.2	k AB								([4a])
						0.1		25	2.20	-2					
						0.2		25	2.48	-2					
						0.4		25	3.06	-2					
						0.6		25	3.64	-2					
			Ac*	A = 0.1-0.2; B = 0.1-0.2			k AB^3	24	5.38	-2				*	([18])
Alkyl substituted Benzene															
.274	.7	$CH_3C_6H_5 + Br_2$	Ac*	A = 0.094	$ZnCl_2$	0.125	k AB	25	3.5	-3				*	([1])
						0.25		25	1.38	-2					
						0.50		25	4.2	-2					
			CCl_4	10^2A = 3-30; 10^2B = 4-10	I_2	0.035	k AB[IBr]	25	8.5	-6				([5]) ([33]) ([36]) *	
.274.1		$CH_3C_6H_5 + HOBr$	Di 50*	10^3A = 5-17; 10^4B = 8-18	$HClO_4$	0.002-0.01	k AB[H^+]	25	2.2	+1					([14b])
.274.2		$CH_3C_6H_5 + ICl$	Ac 99*	A = 0.2; 10^3B = 3-7	$ZnCl_2$	1.40	k AB[$ZnCl_2$]	25	1.8	-5					([26a])
			CF_3COOH	A = 0.24; 10 B = 4			k AB	2	1.14	-3					([1a])
				0.22 4				25	7.5	-3	13				
				0.11 3.8				25	1.20	-2					
				0.056 4-15				25	1.44	-2					
.275	.9	$C_2H_5C_6H_5 + Br_2$	Ac*	10^2A = 4-9	$ZnCl_2$	0.125	k AB	25	3.2	-3				*	([1])
						0.25		25	1.38	-2					
						0.50		25	3.5	-2					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.276		$n\text{-}C_3H_7C_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 24,900		% reacted 10			*	(5)
.277	.11	$(CH_3)_2CHC_6H_5 + Br_2$	Ac*	10^2A = 5-9	$ZnCl_2$	0.125	k AB	25	2.08	-3				*	(1)
						0.25		25	8.3	-3					
						0.50		25	2.04	-2					
.278		$n\text{-}C_4H_9C_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 23,400		% reacted 10			*	(5)
.279		$(CH_3)_2CHCH_2C_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	37,200		10			*	(5)
.280	.13	$(CH_3)_3CC_6H_5 + Br_2$	Ac*	A = 0.095	$ZnCl_2$	0.25		25	6.7	-3				*	(1)
						0.50		25	2.84	-2					
.281		$C_2H_5(CH_3)CHC_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 42,600		% reacted 10			*	(5)
.282		$n\text{-}C_5H_{11}C_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	26,400		10			*	(5)
.283		$(CH_3)_3CCH_2C_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	66,600		10			*	(5)
.284		$(CH_3)_2CH(CH_3)CHC_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	48,400		10			*	(5)
.285		$C_2H_5(CH_3)_2CC_6H_5 + Br_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	60,000		10			*	(5)
.286		$C_6H_5CH_2C_6H_5 + Br_2$	Ac 80*	A = 0.1; B = 0.05				35	17,500		10			*	(33)
.287	.16	$1,2\text{-}(CH_3)_2C_6H_4 + Br_2$	Ac*	A = 0.097	$ZnCl_2$	0.25	k AB	25	1.18	-1				*	(1)
						0.50		25	2.14	-1					
.287.1		$1,2\text{-}(CH_3)_2C_6H_4 + ICl$	Ac 99*	A = 0.2; 10^3B = 3-7	$ZnCl_2$	0.8	k AB$[ZnCl_2]$	25	1.06	-4					(26a)
						1.4		25	1.80	-4					
						1.4		45	1.39	-3	19	1.3	10		

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.288	.17	$1,3-(CH_3)_2C_6H_4 + Br_2$	Ac*	A = 0.04-0.1	$ZnCl_2$	0.0312	k AB	25	6.4	-3				*	(1)
						0.0625		25	3.02	-2					
						0.125		25	1.02	-1					
.288.1		$1,3-(CH_3)_2C_6H_4 + ICl$	Ac 99*	A = 0.1-0.2; 10^3B = 3-7	$ZnCl_2$	0.40	k AB[$ZnCl_2$]	25	1.18	-3					(26a)
						0.80		25	1.85	-3					
						1.40		25	3.33	-3					
						0.40		45	8.31	-3					
						0.80		45	1.30	-2	18	5	10		
.289		$1,4-(CH_3)_2C_6H_4 + Br_2$	Ac*	A = 0.096	$ZnCl_2$	0.125	k AB	25	1.43	-2				*	(1)
						0.25		25	4.7	-2					
						0.50		25	1.03	-1					
.289.1		$1,4-(CH_3)_2C_6H_4 + ICl$	CF_3COOH	10^2A = 5.2; 10^3B = 4			k AB	25	7.8	-2					(1a)
				2.6 4-8				25	8.8	-2					
				1.3 4				25	1.05	-1					
			Ac 99*	A = 0.2; 10^3B = 4-7	$ZnCl_2$	0.80	k AB[$ZnCl_2$]	25	8.2	-5					(23a)
						1.40		25	1.31	-4					
									time		% reacted				
.290		$1-C_2H_5-4-CH_3C_6H_4 + Cl_2$	Ac 80*	A = 0.25; B = 0.12				25	9,400		20			*	(33)
.291		$1,4-[(CH_3)_3C]_2C_6H_4 + Br_2$	Ac*	A = 0.08	$ZnCl_2$	0.50	k AB	25	1.97	-2				*	(1)
									time		% reacted				
.292		$1,2,4-(CH_3)_3C_6H_3 + Br_2$	Ac*	A = 0.10; B = 0.10				25	144		10			*	(19)
				0.10 0.10				25	390		20				
				0.02 0.01				25	51.2		10				(14a)
			Ac 85*	0.005 0.01				25	18.4		10				

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.292		$1,2,4\text{-}(CH_3)_3C_6H_3 + Br_2$ *(continued)*	Ac*	A = 0.093	$ZnCl_2$	0.0625	k AB	25	5.95	-2				*	(1)
						0.125		25	1.87	-1					
.292.1		$1,2,4\text{-}(CH_3)_3C_6H_3 + ICl$	Ac 99*	A = 0.1; 10^3B = 4-7	$ZnCl_2$	0.40	k AB[$ZnCl_2$]	25	3.97	-3					(26a)
						0.80		25	6.1	-3					
						1.40		25	1.03	-2					
									time		% reacted				
.292.2		$1,2,3\text{-}(CH_3)_3C_6H_3 + Br_2$	Ac*	10^2A = 2; 10^2B = 1					404		10				(14a)
									1045		20				
.293		$1,3,5\text{-}(CH_3)_3C_6H_3 + HOCl$	DiW 50*	10^2A = 1.3; 10^3B = 1.0	$HClO_4$	0.050	k B	25	3.20	-4				*	(17)
				2.5 1.0	$AgClO_4$	0.065		25	4.32	-4					
				3.5 1.0				25	5.37	-4					
							$k = k_o + k'[H^+] + k''[H^+]A$ (see comments)								
.294	.18	$1,3,5\text{-}(CH_3)_3C_6H_3 + Br_2$	Ac*	A = 0.2; 10^3B = 4			$k_1AB + k_2AB^2$	16	k_1 2.2	-4				*	(28) (31)
				" "				16	k_2 1.93	0					(26) (28)
				0.01-0.2 "				25	k_1 4.8	-4	15				
				0.01 "				25	k_2 3.68	0					
				0.05 "				25	k_2 3.43	0					
				0.2 "				25	k_2 2.78	0	6.8				
				0.7 "				25	k_1 3.5	-4					
				0.7 "				25	k_2 1.32	0					
				0.05 "	$NaClO_4$	0.10		25	k_1 1.38	-2	17				
				" "		"		25	k_2 1.10	+1	6.5				
				" "		0.15		25	k_1 1.93	-2					
				" "		"		25	k_2 2.08	+1					
				0.05-0.1 "		0.25		25	k_1 4.02	-2					
				" "		"		25	k_2 3.25	+1					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.294	.18	$1,3,5\text{-}(CH_3)_3C_6H_3 + Br_2$ *(continued)*	Ac*	A = 0.05; 10^3B = 4	NaOAc	0.25	$k_1AB + k_2AB^2$	25	k_1 2	-4				*	(26) (28)
				" "		"		25	k_2 5.83	0					
				" "	$LiClO_4$	0.10		25	k_1 5.8	-3					
				" "		"		25	k_2 1.07	+1					(28)
				" "		0.25		25	k_1 1.25	-2					
				" "		"		25	k_2 3.83	+1					
				" "	LiCl	0.10		25	k_1 1.0	-3					
				" "		"		25	k_2 1.17	+1					
				" "		0.25		25	k_1 2.5	-3					
				" "		"		25	k_2 3.75	+1					
				0.05-0.14 "	$ZnCl_2$	0.001		25	k_1 1.80	-2	7.1				
				" "		"		25	k_2 4.00	0	6.5				
				0.05 "		0.002		25	k_1 3.73	-2					
				" "		"		25	k_2 5.50	0					
				" "		0.004		25	k_1 7.87	-2					
				" "		"		25	k_2 3.33	0					
				" "		0.010		25	k_1 1.95	-1					
				" "		"		25	k_2 5.00	0					
				A = 0.02-0.04	$ZnCl_2$	0.0125	k AB	25	1.72	-1				*	(1)
						0.0313		25	5.55	-1					
				10^3A = 1-2; 10^3B = 4	H_2O	7.4	$k_1AB + k_2AB^2$	25	k_1 6.70	-1					(28)
				" "		"		25	k_2 1.80	+2					
			AcD*	A = 0.19; 10^3B = 5.7			$k_1AB + k_2AB^2$	25	k_1 1.33	-4					(26)
				" "				25	k_2 2.35	0					
				.05 "	$NaClO_4$	0.245		25	k_1 2.0	-2					
				" "		"		25	k_2 1.92	+1					
			Ac 90*	10^3A = 3.4; 10^2B = 1.2				25	k_1 3.85	-1					
				" "				25	k_2 1.92	+2					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.294	.18	$1,3,5\text{-}(CH_3)_3C_6H_3 + Br_2$ *(continued)*	AcD 90*	$10^3A = 3.8$; $10^2B = 1.2$	NaOAc	0.099	$k_1AB + k_2AB^2$	25	k_1 2.97	-1				*	(26)
				" "				25	k_2 2.05	+2					
			C_6H_5Cl	$A = 0.19$; $10^3B = 3.8$			$k\,AB^2$	25	2.46	-1					
				19				25	2.98	-1					
				38				25	3.10	-1					
			AcC 90*	$A = 0.2$; $10^3B = 4$				25	1.33	0					(28)
			AcB 90*	" "				25	1.47	0					
			CCl_4	$A = 0.7$; $10^2B = 1\text{-}2$	H_2O	~50 % sat	$k\,ABM^{\frac{1}{2}}$	17	1.27	-2					(27)
				" "		0 % sat		25	3.0	-4					
				" "		40 % sat		25	2.6	-3					
				" "		80 % sat		25	1.23	-2					
				~0.1 0.5	HBr	0.01-0.06		25	6.8	-3					
						0.26		25	4.5	-3					
						0.31		25	3.7	-3					
					H_2O	~50 % sat		34	4.7	-3	-11				
			CCl_4	$A = 0.2$; $10^3B = 11$	IBr	0.001	$k\,AB[IBr]^2$	14	9.2	+2					(10) (32)
				0.1 9		0.0008		25	9.8	+2					(10)
				0.2 2-19		"		25	9.2	+2					
				0.7 9		"		25	7.3	+2					
				1.4 9		"		25	5.5	+2					
				2.8 9		"		25	3.6	+2					
				0.2 9		0.0004		25	9.7	+2					
				0.2 9		0.002		25	7.8	+2					
				0.2 11		0.001		36	8.2	+2	~0				
.294.1		$1,3,5\text{-}(CH_3)_3C_6H_3 + ICl$	Ac 99*	$A = 0.1$; $10^3B = 7$	$ZnCl_2$	0.06-0.1	$k\,AB[ZnCl_2]$	25	6.1	-2					(26a)
				0.05-0.1 4		0.20		25	7.2	-2					
				0.2 2-8		0.20		25	6.7	-2					
				0.2 4		0.40		25	9.2	-2					
				0.1 4		0.80		25	1.46	-1		4	10		

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.294.1		$1,3,5\text{-}(CH_3)_3C_6H_3 + ICl$ *(continued)*	Ac 99*	$A = 0.1\text{-}0.2;\ 10^3B = 7$	$ZnCl_2$	0.06-0.1	$k\,AB[ZnCl_2]$	45	3.22	-1	16				(26a)
			CCl_4	$10^2A = 71.2;\ 10^3B = 3\text{-}10$			$k\,AB^3$	25	7.37	0					(1a)
				35.6 5				25	2.16	+1					
				14.2 5				25	5.76	+1					
				7.12 3				25	9.34	+1					
				1.02 10				25	1.88	+2					
				0.99 1				46	1.21	+2	-4				
.295		$1,3,5\text{-}(C_2H_5)_3C_6H_3 + Br_2$	Ac*	$10^2A = 2\text{-}4$	$ZnCl_2$	0.0125	$k\,AB$	25	6.3	-2				*	(1)
						0.0312		25	1.94	-1					
.295.1		$1,3,5\text{-}(C_2H_5)_3C_6H_3 + ICl$	Ac 99*	$A = 0.1;\ 10^3B = 4$	$ZnCl_2$	0.40	$k\,AB[ZnCl_2]$	25	1.13	-2					(26a)
						0.80		25	1.83	-2					
.296		$1,3,5\text{-}[(CH_3)_3C]_3C_6H_3 + Br_2$	Ac*	$A = 0.066$	$ZnCl_2$	0.50	$k\,AB$	25	1.7	-3				*	(1)
.296.1		$1,2,3,4\text{-}(CH_3)_4C_6H_2 + Br_2$	Ac*	$10^2A = 2;\ 10^2B = 1.0$					time 63.4 155		% reacted 10 20				(14a)
.297		$1,2,3,5\text{-}(CH_3)_4C_6H_2 + Br_2$	Ac*	$10^2A = 7.4$	$ZnCl_2$	0.0312	$k\,AB$	25	1.23	0				*	(1)
			Ac 90*	$10^3A = 2\text{-}10;$ $10^3B = 9\text{-}3.6$	NaOAc	0.1	$k_1AB + k_2AB^2$								(26)
								25	k_1 8.6 k_2 5.2	-1 +2					
.297.1		$1,2,3,5\text{-}(CH_3)_4C_6H_2 + ICl$	Ac 99*	$A = 0.08;\ 10^3B = 4\text{-}7$	$ZnCl_2$	0.05	$k\,AB[ZnCl_2]$	25	6.13	-2					(26a)
						0.20		25	7.60	-2					
						0.40		25	8.8	-2					

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.297.1		$1,2,3,5\text{-}(CH_3)_4C_6H_2 + ICl_2$	Ac 99*	A = 0.08; 10^3B = 4-7	$ZnCl_2$	0.08	$k\,AB[ZnCl_2]$	25	1.29	-1		1.0	11		(26a)
		(continued)				0.05		45	3.54	-1	16				
.298		$1,2,4,5\text{-}(CH_3)_4C_6H_2 + Br_2$	Ac*	10^2A = 4-8	$ZnCl_2$	0.0312	$k\,AB$	25	6.7	-2				*	(1) (19)
						0.0625		25	2.42	-1					
.298.1		$1,2,4,5\text{-}(CH_3)_4C_6H_2 + ICl$	Ac 99*	10^2A = 7-15;	$ZnCl_2$	0.40	$k\,AB[ZnCl_2]$	25	1.39	-3					(26a)
				10^3B = 4-7		0.80		25	1.87	-3					
						1.40		25	3.14	-3					
						0.78		45	1.25	-2	17	1.0	10		
.299		$(CH_3)_5C_6H + Br_2$	Ac*	A = 0.011	$ZnCl_2$	0.0312	$k\,AB$	25	2.35	0				*	(1)
			Ac 90*	10^3A = 3-11;	NaOAc	0.1	$k_1AB + k_2AB^2$								(26)
				10^3B = 1-4				25	k_1 1.81	0					
								25	k_2 1.86	+3					
.300		$(CH_3)_5C_6H + ICl \longrightarrow$	Ac*	A = B = 0.01-0.02				24						*	(29)
		$(CH_3)_5C_6I$, $(CH_3)_5C_6Cl$, HCl, HI													
		(75%) (25%)	Ac 99*	10^2A = 5-20;	$ZnCl_2$	0.056	$k\,AB[ZnCl_2]$	25	2.91	-2					(26a)
				10^3B = 2-7		0.11		25	3.04	-2					
						0.21		25	3.73	-2					
						0.40		25	4.23	-2					
						0.82		25	6.10	-2		5	10		
						0.055		45	1.67	-1					
						0.11		45	1.73	-1	16				
			CCl_4	10^3A = 244; 10^3B = 5			$k\,AB^3$	25	4.92	-1					(1a)
				97 2-7				25	1.65	0					
				49 3				25	3 18	0					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.300		$(CH_3)_5C_6H + ICl \longrightarrow$ *(continued)*	CCl_4	$10^2A = 8.6$; $10^3B = 9$			$k\,AB^2$	25	6.20	0					([1a])
				8.4 8				46	5.2	0	-2				
Alkoxy(Hydroxy)-substituted benzene															
.301		$C_6H_5OH + HOCl$	H_2O	$10^3A = 9$; $10^4B = 5$	$HClO_4$	1.2	$k\,B$; $k = k_o + k'[H^+] + k''[H^+]A$							*	([17])
				" "	$AgClO_4$	0.008		25	2.27	-4					
				" "	"	0.016		25	1.90	-4					
				" "	"	0.04		25	1.93	-4					
				" "	"	0.08-0.16		25	1.82	-4					
				2 10	$AgClO_4$	0.027		25	2.28	-4					
				6 10	$HClO_4$	0.05		25	3.67	-4					
				10 10	"	"		25	4.25	-4					
				18 10	"	"		25	6.68	-4					
				3-8 20	H_2SO_4 Ag^+	0.011 0.005-0.1		25	3.1	-4					([15])
				2 10	HCl	0.0002	$k\,B[HCl]^2$	25	3.57	+4					([34])
.302		$C_6H_5O^- + HOCl$	H_2O	$10^3A = 2-10$; $10^4B = 10$	NaOH	0-0.1	$k\,AB$	25	5.5	+3				*	([34])
									time		% reacted				
.303		$C_6H_5OH + Br_2$	Ac*	$A = B = 0.001$	H_2SO_4	0-0.07		25	48		20			*	([33])
									198		50				

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.304	$C_6H_5OH + I_2$	H_2O	A=0.01; B=0.001	HOAc	pH	k AB; $k = k_o + k_1[HOAc]$							*	(30) (34)
				NaOAc	4.66		25	k_o 2.90	-4					
				"	"		25	k_1 3.66	-3					
				"	4.96		25	k_o 5.56	-4					
				"	"		25	k_1 1.46	-2					
				"	5.26		25	k_o 1.10	-3					
				"	"		25	k_1 5.96	-2					
				$H_2PO_4^-$		k AB; $k = k_o + k_1[H_2PO_4^-]$								
				$HPO_4^=$	6.00		25	k_o 6.7	-5					
				"	"		25	k_1 3.3	-4					
				"	6.40		25	k_o 1.5	-4					
				"	"		25	k_1 2.2	-3					
				"	6.70		25	k_o 3.0	-4					
				"	"		25	k_1 8.0	-3					
				"	7.12		25	k_o 9.5	-4					
				"	"		25	k_1 6.1	-2					
			10^3A= 8; 10^3B= 2	KH_2PO_4 / Na_2HPO_4	0.024 / 0.008	k AB	25	1.20	-2				*	(3)
			ionic strength=0.30	"	0.045 / 0.015		25	1.57	-2					
				"	0.60 / 0.020		25	1.85	-2					
				"	0.032 / 0.008		25	9.17	-3					
				"	0.064 / 0.016		25	1.26	-2					
				"	0.080 / 0.020		25	1.42	-2					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.304	$C_6H_5OH + I_2$ *(continued)*	H_2O	$10^3A = 8$; $10^3B = 2$	KH_2PO_4	0.032	k AB	35	3.78	-2	25			*	([3])
				Na_2HPO_4	0.008									
			ionic strength = 0.30	"	0.048		35	4.57	-2					
					0.012									
				"	0.080		35	6.07	-2					
					0.020									
				"	0.050		35	1.24	-2					
					0.005									
				"	0.10		35	1.87	-2					
					0.010									
				HOAc	0.010		25	1.11	-2					
				NaOAc	0.10									
				"	0.016		25	1.48	-2					
					0.16									
		Ac 10*	$10^3A = 8$; $10^3B = 4$	NaOAc	1.0		25	1.50	-2					([7])
		M 30*	8 2	KH_2PO_4	0.025		25	1.20	-2					
				Na_2HPO_4	0.012									
		Di 30*	8 2	"	0.02		25	1.30	-3					
					0.01									
.305	$C_6H_5OCH_3 + HOCl$	H_2O	$10^3A = 3$-10; $10^3B = 2$	Ag^+ +	0.005-0.1	k B								
				H_2SO_4	0.011		25	3.1	-4				*	([15])
			6.6 0.5	$HClO_4$	0.009		25	1.1	-4					([17])
			3-10 0.5	"	0.012		25	1.43	-4					
			7.7 1.0	"	0.012		25	1.63	-4					
			" 2.0	"	0.012		25	2.68	-4					

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.305		$C_6H_5OCH_3 + HOCl$ *(continued)*	H_2O	$10^3A = 7.7$; $10^3B = 6.0$	$HClO_4$	0.012	kB	25	7.02	-4				*	(17)
				" 12.0	"	0.012		25	1.06	-3					
				3 8	"	0.1		25	6.3	-4					(16)
				6.6 0.2-1	"	0.6		25	1.3	-3					(17)
				10 1	HCl	0.0002	$kB[HCl]^2$	25	3.57	+4					(34)
			D1W 50*	$10^3A = 6.6$; $10^4B = 7$	$AgClO_4$ + $HClO_4$	0.16 / 0.012	kB	0	5.00	-5				*	(17)
				" "	"	"		25	1.55	-4					
				8.0 5	"	0.065 / 0.05		25	2.35	-4					
				15 5	"	"		25	2.65	-4					
				28 5	"	"		25	3.25	-4					
				6.6 7	"	0.16 / 0.012		35	2.75	-4					
.306	.19	$C_6H_5OCH_3 + Br_2$	Ac*	$10^2A = 2.5$; $10^2B = 1$	NaOAc LiBr	0.068 / 0.035	kAB	25	1.6	-2				*	(33)
									time		% reacted				
				A = B = 0.00625				25	84		10				(19)
									222		20				
.307		$C_6H_5OCH_3 + ICl \longrightarrow$	Ac*	A = B = 0.0125				24	12,960		10			*	(29)
		p-$IC_6H_4OCH_3$, p-$ClC_6H_4OCH_3$,	HCl, HI	0.025				24	2,790		10				
		(85 %) (15 %)		0.05				24	708		10				
				0.0125				40	4,620		10				
				0.025				40	1,140		10				
				0.05				40	288		10				
.308		$C_6H_5OC_2H_5 + HOCl$	H_2O	$10^3A = 4$; $10^3B = 1$	HCl	0.0002	$kB[HCl]^2$	25	3.60	+4				*	(34)

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
									time		% reacted				
.308.1		$C_6H_5OC_2H_5 + Br_2$	Ac*	A = 0.01; 10^3B = 1			k AB	20	86.5		20				(1b)
.308.2		$C_6H_5OCH(CH_3)_2 + Br_2$	Ac*	A = 0.01; 10^3B = 1			k AB	20	143		20				(1b)
.308.3		$C_6H_5OC(CH_3)_3 + Br_2$	Ac*	A = 0.01; 10^3B = 1			k AB	20	390		20				(1b)
.309		$C_6H_5OC_6H_5 + Br_2$	Ac*	A = B = 0.0125				25	2,700		10			*	(33)
Carboxyl substituted benzene															
.310		$C_6H_5COOH + HOBr$	Ac 40*	10^3A ≃ 8; 10^3B = 3-4	$HClO_4$	0.118	k AB	22	5.1	-3					(20)
						0.224		22	1.2	-2					
						0.448		22	3.6	-2					
						0.7		22	8.8	-2					
						0.9		22	1.7	-1					
					$HClO_4$, $NaClO_4$	0.224, 0.672		22	2.42	-2					
					"	0.448, 0.448		22	5.47	-2					
					H_2SO_4	0.294		22	1.63	-2					
						0.59		22	4.8	-2					
						1.17		22	2.55	-1					
									time		% reacted				
.311		$C_6H_5COOC_6H_5 + Cl_2$	Ac*	A = 0.10; B = 0.01				25	46,000		10			*	(33)
.312		$C_6H_5COOC_2H_5 + Cl_2$	Ac 80*	A = 0.5; B = 0.05				25	480		10			*	(33)
Amine (Amide)-substituted benzene															
.313		$C_6H_5NH_2 + I_2 \longrightarrow (p)$	H_2O	10^3A = 2-8; 10^3B = 1-4 ionic strength = 0.3 KI = 0.12	KH_2PO_4, Na_2HPO_2	0.01, 0.01	k AB	25	6.98	-3				*	(2)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.313		$C_6H_5NH_2 + I_2 \longrightarrow (p)$ *(continued)*	H_2O	$10^3A = 2\text{-}8$; $10^3B = 1\text{-}4$	KH_2PO_4	0.03-0.002	k AB	25	1.18	-2				*	(2)
					Na_2HPO_2	0.02									
					"	0.04-0.003		25	1.68	-2					
						0.03									
					"	0.03		25	2.43	-2					
						0.045									
				KI = 0.12 ionic strength = 0.3			$k = k_o + k_1[HPO_4^{=}] + k_2[H_2PO_4^{-}]$								
								25	k_o 2.05	-3					
								25	k_1 4.88	0					
								25	k_2 5.0	-3					
								35	k_o 7.58	-3	24				(3)
								35	k_1 1.48	+1	20				
			H_2O	$10^3A = 2\text{-}8$; $10^3B = 1\text{-}4$	KI	0.1	k AB	25	3.46	-2				*	(2)
				$KH_2PO_4 = 0.05$ $Na_2HPO_4 = 0.05$	ionic strength = 0.8	0.15		25	1.52	-2					
						0.2		25	8.58	-3					
						0.3		25	3.82	-3					
						0.4		25	2.15	-3					
						0.5		25	1.38	-3					
			M 30*	$10^3A = 8$; $10^3B = 1$	Na_2HPO_4	0.02	k AB	25	1.81	-2				*	(6)
					KH_2PO_4	0.005									
					"	0.03		25	2.50	-2					
						0.075									
					"	0.05		25	3.93	-2					
						0.0125									
				KI = 0.05 ionic strength = 0.28			$k = k_o + k_1[HPO_4^{=}]$								
								25	k_o 3.90	-3					
								25	k_1 7.07	-1					

No	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
								time		% reacted				
.314	$CH_3CONHC_6H_5 + ICl \longrightarrow$	Ac*	A = B = 0.025				24	46,800		10			*	(29)
	$CH_3CONHC_6H_4I$, $CH_3CONHC_6H_4Cl$, + HCl, HI		0.05				24	9,600		10				
	(90 %) (10 %)		0.025				50	6,300		10				
			0.05				50	2,160		10				
.315	$CH_3CON(CH_3)C_6H_5 + Br_2$	Ac*	A = B = 0.05				25	10,900		10			*	(33)
	Sulfo-alkyl substituted benzene													
.316	$C_6H_5CH_2SO_3Na + HOCl$	H_2O	$10^2A = 1-7$; $10^3B \simeq 4$	$HClO_4$	2.0	k AB	22	1.0	-3					(21)
					30		22	3.5	-3					
					4.0		22	1.0	-2					
				H_2SO_4	1.18		22	1.85	-3					
					2.25		22	9.16	-3					
					3.0		22	2.9	-2					
				H_2SO_4 + KCl	2.25									
					0.0001		22	1.21	-2					
				"	0.0004		22	2.01	-2					
				"	0.0006		22	2.6	-2					
.317	$C_6H_5CH_2SO_3Na + HOBr$	H_2O	$10^3A = 7-14$; $10^3B = 3-5$	$HClO_4$	0.0047	k AB	22	7.23	-2					(20)
					0.0094		22	1.46	-1					
					0.024		22	3.4	-1					
					0.047		22	6.7	-1					
					0.094		22	1.28	0					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Disubstituted Benzene													
	Alkyl, Hydroxyl (Alkoxyl)													
.318	$o\text{-}CH_3C_6H_4O^- + HOCl$	H_2O	$10^3A = 2\text{-}10;\ 10^3B \simeq 1$	NaOH	0-0.01	$k\,AB$	25	2.08	+4				*	(34)
.319	$m\text{-}CH_3C_6H_4O^- + HOCl$	H_2O	$10^3A = 2\text{-}10;\ 10^3B \simeq 1$	NaOH H^+	0-0.5 3×10^{-6}	$k\,AB$	25 25	7.3 5.8	+4 +4				*	(34)
.320	$p\text{-}CH_3C_6H_4O^- + HOCl$	H_2O	$10^3A = 2\text{-}10;\ 10^3B \simeq 1$ ~ 2 1	NaOH HCl	0-0.01 0.0002	$k\,AB$ $k\,B[HCl]^2$	25 25	1.50 3.62	+4 +4				*	(34)
.321	$4\text{-}CH_3C_6H_4OH + I_2 \longrightarrow (2)$	Ac 10*	$10^3A = 8;\ 10^3B = 4$	NaOAc KI	1 0.03	$k\,AB$	25	1.97	-2				*	(7)
				KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	2.38	-2					
				KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12		25	1.33	-2					
		Di 30*	$10^3A = 8;\ 10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1	$k\,AB$	25	1.45	-3				*	(7)
.322	$m\text{-}CH_3C_6H_4OCH_3 + HOCl$	DiW 50*	$10^3A =$	$AgClO_4$ $HClO_4$		$k\,B;\ k = k_o + k'[H^+] + k''[H^+]A$							*	(17)
			5		0.012		25	2.2	-4					
			10		"		25	2.8	-4					
			15		"		25	3.5	-4					
.322.0	$m\text{-}CH_3C_6H_4OCH_3 + Br_2$	Ac*	$10^2A = 1;\ 10^3B = 1$			$k\,AB$	20	2.2	-1					(1b)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.323	p-$CH_3C_6H_4OCH_3$ + HOCl	D1 62,5*	10^2A= 4.4; 10^4B= 8	$HClO_4$ $AgClO_4$	0.50 0.05	$k\,B[H^+]$	25	8.2	-4				*	([35])
		D1W 50*	5-8 10	$HClO_4$ $AgClO_4$	0.05 0.027	$k\,B$; $k = k_o + k'[H^+] + k''[H^+]A$							*	([17])
							25	1.9	-4					
.324	p-$CH_3C_6H_4OCH_3$ + DOCl	D1D 62*	A= 0.044; 10^4B= 8	$HClO_4$ $AgClO_4$	0.50 0.05	$k\,B[H^+]$	25	1.58	-3				*	([35])
.325	p-$CH_3C_6H_4OCH_3$ + ICl ⟶ 2-I-4-$CH_3C_6H_3OCH_3$, 2-Cl-4-$CH_3C_6H_3OCH_3$, HCl, HI (50 %) (50 %)	Ac*	A = B = 0.0125 0.025 0.05				24 24 24	time 83,400 25,200 516		% reacted 20 20 20			*	([29])
.326	p-$C_2H_5C_6H_4OH$ + I_2 ⟶ (2)	Ac 10*	10^3A= 8; 10^3B= 4	NaOAc KI	1 0.03	$k\,AB$	25	2.40	-2				*	([7])
		M 25*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	2.80	-2					
		M 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12		25	1.51	-2					
		D1 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	1.50	-3					
.327	4-$CH_3CH_2CH_2C_6H_4OH$ + I_2 ⟶ (2)	Ac 10*	10^3A= 8; 10^3B= 4	NaOAc KI	1 0.03	$k\,AB$	25	2.38	-2				*	([7])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.327	$4\text{-}CH_3CH_2CH_2C_6H_4OH + I_2 \longrightarrow (2)$ *(continued)*	M 30*	$10^3A = 8$; $10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12	k AB	25	1.57	-2				*	(7)
.328	$4\text{-}(CH_3)_2CHC_6H_4OH + I_2 \longrightarrow (2)$	Ac 10*	$10^3A = 8$; $10^3B = 4$	NaOAc KI	1 0.03	k AB	25	2.82	-2				*	(7)
		M 25*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	3.18	-2					
		M 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12		25	1.76	-2					
		Di 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	1.58	-3					
.329	$4\text{-}(n\text{-}C_4H_9)C_6H_4OH + I_2 \longrightarrow (2)$	M 30*	$10^3A = 8$; $10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12	k AB	25	1.60	-2				*	(7)
.330	$4\text{-}C_2H_5(CH_3)CHC_6H_4OH + I_2 \longrightarrow (2)$	M 30*	$10^3A = 8$; $10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12	k AB	25	1.80	-2				*	(7)
.331	$4\text{-}(CH_3)_3CC_6H_4OH + I_2 \longrightarrow (2)$	Ac 10*	$10^3A = 8$; $10^3B = 4$	NaOAc KI	1 0.03	k AB	25	3.60	-2				*	(7)
		M 25*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	4.05	-2					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.331	$4\text{-}(CH_3)_3CC_6H_4OH + I_2 \longrightarrow (2)$ *(cont.)*	M 30*	$10^3A = 8$; $10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12	k AB	25	2.27	-2				*	(7)
		D1 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1		25	1.90	-3					
.332	$4\text{-}C_2H_5(CH_3)_2CC_6H_4OH + I_2 \longrightarrow (2)$	M 30*	$10^3A = 8$; $10^3B = 2$	KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12	k AB	25	2.72	-2				*	(7)
	Disubstituted Benzene **Di-Alkoxyl**													
.333	$o\text{-}(CH_3O)_2C_6H_4 + Br_2$	Ac*	A = B = 0.0031				25 25	time 91.3 221		% reacted 10 20			*	(19)
.334	$p\text{-}(CH_3O)_2C_6H_4 + HOCl$	H_2O	$10^3A = 4$; $10^3B = 2$	H_2SO_4 Ag^+	0.011 0.005-0.1	k B	25	3.1	-4				*	(15)
.335	$p\text{-}(CH_3O)_2C_6H_4 + Br_2$	Ac*	A = B = 0.0125 " 0.00625				25 25 25 25	time 336 763 1,220 2,730		% reacted 10 20 10 20			*	(19)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Disubstituted Benzene Alkoxyl, Carboxyl														
.336	p-$CH_3OC_6H_4COONa$ + HOBr	H_2O	$10^3A = 7-14$; $10^3B = 4-5$	Na_2HPO_4, KH_2PO_4	0.01-0.03	k AB							*	(20)
				"	0.002		22	1.1	-1					
				"	0.004		22	1.6	-1					
				"	0.006		22	2.2	-1					
				Na_2HPO_4, KH_2PO_4, KBr	0.011, 0.002, 0.0017	k AB	22	1.32	0					
Disubstituted Benzene Alkyl, Amino														
.337	4-$CH_3C_6H_4NH_2$ + I_2 ⟶ (2)	M 30*	$10^3A = 8$; $10^3B = 1$	Na_2HPO_4	0.02	k AB	25	3.37	-3				*	(6)
					0.04		25	4.25	-3					
					0.06		25	5.27	-3					
					0.08		25	6.29	-3					
					0.02		35	1.12	-2					
					0.04		35	1.43	-2					
				$[KI] = 0.05$, $[Na_2HPO_4]/[KH_2PO_4] = 4$, $\mu = 0.28$	0.06		35	1.75	-2					
					0.08		35	2.08	-2					
						$k = k_o + k_1[Na_2HPO_4]$								
							25	k_o 2.35	-3					
							25	k_1 4.89	-2					
							35	k_o 7.94	-3	22	5	13		
							35	k_1 1.59	-1	22	3	14		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.338	$4\text{-}C_2H_5C_6H_4NH_2 + I_2 \longrightarrow$ (2)	M 30*	$10^3A = 8$; $10^3B = 1$ $\mu = 0.28$	Na_2HPO_4	0.04	k AB	25	4.76	-3				*	(6)
				KH_2PO_4	0.01		35	1.54	-2					
				KI	0.05									
.339	$4\text{-}(CH_3)_2CHC_6H_4NH_2 + I_2 \longrightarrow$ (2)	M 30*	$10^3A = 8$; $10^3B = 1$ $\mu = 0.28$	Na_2HPO_4	0.04	k AB	25	5.12	-3				*	(6)
				KH_2PO_4	0.01		35	1.60	-2					
				KI	0.05									
.340	$4\text{-}(CH_3)_3CC_6H_4NH_2 + I_2 \longrightarrow$ (2)	M 30*	$10^3A = 8$; $10^3B = 1$	Na_2HPO_4	0.02	k AB	25	5.97	-3				*	(6)
				$[KI] = 0.05$	0.04		25	7.02	-3					
				$[Na_2HPO_4]/[KH_2PO_4] = 4$	0.06		25	8.06	-3					
				$\mu = 0.28$	0.08		25	8.96	-3					
					0.02		35	1.74	-2					
					0.04		35	2.04	-2					
					0.06		35	2.39	-2					
					0.08		35	2.72	-2					
						$k = k_o + k_1[Na_2HPO_4]$								
							25	k_o 4.90	-3					
							25	k_1 5.30	-2					
							35	k_o 1.40	-2	19	5	11		
							35	k_1 1.66	-1	21	9	14		
	Disubstituted benzene													
	Hydroxyl, Nitro													
.341	$o\text{-}NO_2C_6H_4O^- + HOCl$	H_2O	$10^3A = 2\text{-}10$; $10^3B = 1$	NaOH	0.015	k AB	25	1.68	+1				*	(34)
.342	$m\text{-}NO_2C_6H_4O^- + HOCl$	H_2O	$10^3A = 2\text{-}10$; $10^3B = 1$	NaOH	0-0.01	k AB	25	9.8	+1				*	(34)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k	n		A^o	n		
.343	m-$NO_2C_6H_4OH + Br_2$	H_2O	$10^5B = 5$-25	Ag_2SO_4	sat.	k AB	25	~9	+3				*	(22)
.344	m-$NO_2C_6H_4OH + HOBr$	H_2O	A = B = 0.01-0.3	Ag_2SO_4	sat.	k AB	25	~1.0	+1				*	(22)
.345	p-$NO_2C_6H_4O^- + HOCl$	H_2O	$10^3A = 2$-10; $10^3B = 1$	NaOH	0.015	k AB	25	1.14	+1				*	(34)
				HCl	0.0002	k B[HCl]^2	25	3.44	+4					
Disubstituted benzene Hydroxyl, Halogen														
.346	o-$ClC_6H_4O^- + HOCl$	H_2O	$10^3A = 2$-10; $10^3B \simeq 1$	NaOH	0.1	k AB	25	9.8	+2				*	(34)
.347	p-$ClC_6H_4O^- + HOCl$	H_2O	$10^3A = 2$-10; $10^3B \simeq 1$	NaOH	0-0.01	k AB	25	8.2	+2				*	(34)
Disubstituted benzene Alkoxyl, Nitro														
.348	o-$NO_2C_6H_4OCH_3 + Cl_2$	Ac 99*	$10^2A = 5$; $10^3B = 5$	HCl	0.02	k AB	20	3.00	-4				*	(25)
.349	p-$NO_2C_6H_4OCH_3 + HOBr$	H_2O	$10^3A = 5$; $10^3B \sim 6$			k AB	20	2.1	-2				*	(13)
		AcW 10*					20	1.83	-1					
		AcW 25*					20	1.92	-1					
		AcW 50*					20	1.89	-1					
		AcW 65*					20	1.79	-1					
		AcW 75*					20	1.62	-1					
				H_2SO_4	0.005		20	2.48	-1					
					0.010		20	3.24	-1					
					0.017		20	4.34	-1					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.349	p-$NO_2C_6H_4OCH_3$ + HOBr *(continued)*	AcW 75*	$10^3A = 5$; $10^3B \sim 6$	H_2SO_4	0.030	k AB	20	6.60	-1				*	(13)
					0.043		20	8.20	-1					
					0.088		20	1.61	0					
						$k = k_o + k_1[H_2SO_4]$								
							20	k_1 1.64	+1					
				Na_2HPO_4	0.005		20	1.64	-1					
				Na_2SO_4	0.020		20	1.70	-1					
				Li_2SO_4	0.030		20	1.76	-1					
				NaOAc	0.010		20	1.35	-1					
					0.050		20	1.22	-1					
					sat.		20	8.5	-2					
		AcW 85*					20	1.35	-1					
.350	o-$NO_2C_6H_4OC_2H_5$ + Cl_2	Ac 99*	$10^2A = 5$; $10^3B = 5$	HCl	0.020	k AB	20	6.03	-4				*	(25)
.351	4-$NO_2C_6H_4OC_2H_5$ + HOBr $\longrightarrow$ (2)	Ac 75*	$10^3A = 2$-8; $10^3B = 3$-8			k AB	20	3.29	-1				(11) (13) (14)	
.352	o-$NO_2C_6H_4OCH_2CH_2CH_3$ + Cl_2	Ac 99*	$10^2A = 5$; $10^3B = 5$	HCl	0.020	k AB	20	6.90	-4				*	(25)
.353	p-$NO_2C_6H_4OCH_2CH_2CH_3$ + HOBr	Ac 75*	$10^3A = 2$-10; $10^3B = 2$-10			k AB	20	3.53	-1					(14)
.354	p-$NO_2C_6H_4OCH(CH_3)_2$ + HOBr	Ac 75*	$10^3A = 2$-10; $10^3B = 2$-10			k AB	20	6.42	-1					(14)
.355	p-$NO_2C_6H_4O(CH_2)_3CH_3$ + HOBr	Ac 75*	$10^3A = 2$-10; $10^3B = 2$-10			k AB	20	3.60	-1					(14)
.356	p-$NO_2C_6H_4O(CH_2)_4CH_3$ + HOBr	Ac 75*	$10^3A = 2$-10; $10^3B = 2$-10			k AB	20	3.59	-1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Disubstituted Benzene													
	Aryl alkoxyl, Nitro													
.357	p- $NO_2C_6H_4OCH_2C_6H_5$ + HOBr	Ac 75*	10^2A= 1-2; 10^3B= 5-8			k AB	20	1.14	-1				*	(11) (13) (14)
	Disubstituted Benzene													
	Amino(Amide), Nitro													
.358	m-$NO_2C_6H_4N(CH_3)_2$ + Br_2	Ac*	10^3A= 1; 10^4B = 1	NaOAc LiBr	0.068 0.035	k AB	25	1.42	+1				*	(33)
.359	m-$NO_2C_6H_4NHCOCH_3$ + Cl_2	Ac*	A = 0.1; B = 0.07			k AB	25	6.7	-5				*	(33)
	Disubstituted Benzene													
	Alkoxyl, Halogen													
.360	p-$FC_6H_4OCH_2COOH$ + HOBr	AcW75*				k AB	20	9.5	0					(14)
.361	o-$ClC_6H_4OCH_3$ + Br_2	AcW75*	10^3A= 7.5; 10^2B= 1.5			k AB + k' AB^2	20	5.52	-2				*	(9)
					HBr	0.0075	20	5.37	-2					
						0.0375	20	4.50	-2					
							k'/k	6.35	+1					
.362	p-$ClC_6H_4OCH_3$ + Br_2	Ac 50*	10^2A= 4-8; 10^3B= 7.5			k AB	20	1.12	-2				*	(12)
		AcW75*	A = B = 0.02			k AB + k' AB^2	20	2.28	-4					(11)
							k'/k	3.19	+2					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.363	p-$ClC_6H_4OC_2H_5 + Br_2$	Ac 50*	$10^2A = 4$-8; $10^3B = 7.5$			k AB	20	2.55	-2				*	(12)
		AcW75*	A = B = 0.02			k AB + k' AB^2	20	5.68	-4					(11)
							k'/k	3.19	+2					
.364	p-$ClC_6H_4OCH_2CH_2CH_3 + Br_2$	AcW75*	A = B = 0.02			k AB + k' AB^2	20	7.45	-4				*	(11)
							k'/k	3.19	+2					
.365	p-$ClC_6H_4OCH(CH_3)_2 + Br_2$	Ac 50*	$10^2A = 4$-8; $10^3B = 7.5$			k AB	20	8.0	-2				*	(12)
		AcW75*	$10^2A = 2$-4; $10^2B = 2$			k AB + k' AB^2	20	1.91	-3					(11)
			$10^3A = 7.5$; $10^2B = 4$	HBr	0.0075		20	1.83	-3					
			" "		0.0225		20	2.00	-3					
			" "		0.0375		20	2.17	-3					
			" "		0.075		20	2.57	-3					
							k'/k	3.19	+2					
.366	p-$ClC_6H_4OCH_2COOH + HOBr$	AcW75*				k AB	20	4.1	0					(14)
.367	p-$ClC_6H_4OCH_2CH_2COOH + HOBr$	AcW75*				k AB	20	3.5	+1					(14)
.368	p-$ClC_6H_4OCH(CH_3)COOH + HOBr$	AcW75*				k AB	20	5.0	0					(14)
.369	p-$BrC_6H_4OCH_3 + Br_2$	Ac 50*	$10^2A = 4$-8; $10^3B = 7.5$			k AB	20	1.20	-2				*	(12)
.370	p-$BrC_6H_4OC_2H_5 + Br_2$	Ac 50*	$10^2A = 4$-8; $10^3B = 7.5$			k AB	20	2.80	-2				*	(12)
.371	p-$BrC_6H_4OCH(CH_3)_2 + Br_2$	Ac 50*	$10^2A = 4$-8; $10^3B = 7.5$			k AB	20	8.49	-2				*	(12)
.372	p-$BrC_6H_4OCH_2COOH + HOBr$	AcW75*				k AB	20	5.6	0					(14)
.373	p-$BrC_6H_4OCH_2CH_2COOH + HOBr$	AcW75*				k AB	20	5.1	1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Disubstituted benzene Aryl-alkoxyl, Halogen													
.374	p-(o-$NO_2C_6H_4CH_2O$)C_6H_4F + Cl_2	Ac 99*	A = 3B ~ 10^{-2}	HCl		k AB	20	5.00	-3				*	(24)
.375	p-(o-$NO_2C_6H_4CH_2O$)C_6H_4F + HOBr	AcW75*				k AB	20	1.56	+1					(14)
.376	p-(o-$NO_2C_6H_4CH_2O$)C_6H_4Cl + Cl_2	Ac 99*	A = 3B ~ 10^{-2}	HCl		k AB	20	2.97	-3				*	(24)
.377	p-(o-$NO_2C_6H_4CH_2O$)C_6H_4Cl + HOBr	AcW75*				k AB	20	9.5	0					(14)
.378	p-(p-$NO_2C_6H_4CH_2O$)C_6H_4Cl + HOBr	AcW75*				k AB	20	1.17	+1					(14)
.379	p-(2',6'-$Cl_2C_6H_3CH_2O$)C_6H_4Cl + Cl_2	Ac 99*	A = 3B ~ 10^{-2}	HCl		k AB	20	4.58	-3				*	(24)
.380	p-(o-$CH_3C_6H_4CH_2O$)C_6H_4Br + Cl_2	Ac 99*	A = 3B ~ 10^{-2}	HCl		k AB	20	1.83	-2				*	(24)
	Disubstituted benzene Amino, Halogen													
.381	4-$ClC_6H_4NH_2$ + ICl ⟶ 4-Cl-2-$IC_6H_3NH_2$ + HCl	H_2O	10^3A = 4; 10^3B = 1	$HClO_4$	0.4	k AB	11	1.48	-2				*	(4)
				NaCl	0.4		18	2.86	-2					
							25	5.61	-2					
							35	1.37	-1	16.5	7	10		
			4-5 1	$HClO_4$	1.0		25	2.27	-1					
				NaCl = 0.1	2.0		25	5.80	-2					
					3.0		25	1.61	-2					
					4.0		25	4.27	-3					
					5.0		25	1.07	-3					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.381	$4\text{-}ClC_6H_4NH_2 + ICl \longrightarrow$	H_2O	$10^3A = 5$; $10^3B = 1$	NaCl	0.2	k AB	25	4.23	-1				*	([4])
	$4\text{-}Cl\text{-}2\text{-}IC_6H_3NH_2 + HCl$ *(continued)*				0.3		25	1.97	-1					
				$HClO_4$ = 0.20	0.4		25	1.16	-1					
				μ = 1.00	0.5		25	7.68	-2					
					0.6		25	5.55	-2					
					0.7		25	4.35	-2					
					0.8		25	3.43	-2					
			4 1	$HClO_4$	0.4									
				NaCl	0.4									
				$NaClO_4$	μ = 0.8		25	5.62	-2					
					1.0		25	5.35	-2					
					1.2		25	5.05	-2					
					1.4		25	4.70	-2					
					1.6		25	4.35	-2					
					1.8		25	3.98	-2					
					2.0		25	3.65	-2					
	Disubstituted benzene													
	Aryl (diphenyl), alkoxyl													
.382	$p\text{-}C_6H_5C_6H_4OCH_3 + Cl_2$	Ac 99*	$10^3A = 5$; $10^3B = 2.5$	HCl	0.01	k AB	20	1.24	0				*	([25])
			10 5		0.02		20	1.27	0					
.383	$2'\text{-}NO_2C_6H_4C_6H_4\text{-}4\text{-}OCH_3 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	3.72	-1				*	([25])
.384	$4'\text{-}NO_2C_6H_4C_6H_4\text{-}4\text{-}OCH_3 + Cl_2$	Ac 99*	$10^3A = 5$; $10^3B = 2.5$	HCl	0.01	k AB	20	1.32	-1				*	([25])
			10 5		0.02		20	1.38	-1					
.385	$p\text{-}C_6H_5C_6H_4OC_2H_5 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	2.60	0				*	([25])

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.386	2'-$NO_2C_6H_4C_6H_4$-4-OC_2H_5 + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	7.18	-1				*	(25)
.387	4'-$NO_2C_6H_4C_6H_4$-4-OC_2H_5 + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	2.61	-1				*	(25)
.388	*p*-$C_6H_5C_6H_4OCH_2CH_2CH_3$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	2.72	0				*	(25)
.389	2'-$NO_2C_6H_4C_6H_4$-4-$OCH_2CH_2CH_3$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	7.98	-1				*	(25)
.390	4'-$NO_2C_6H_4C_6H_4$-4-$OCH_2CH_2CH_3$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	2.83	-1				*	(25)
.391	*p*-$C_6H_5C_6H_4OCH(CH_3)_2$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	4.72	0				*	(25)
.392	2'-$NO_2C_6H_4C_6H_4$-4-$OCH(CH_3)_2$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	1.55	0				*	(25)
.393	4'-$NO_2C_6H_4C_6H_4$-4-$OCH(CH_3)_2$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	5.48	-1				*	(25)
.394	*p*-$C_6H_5C_6H_4O(n\text{-}C_4H_9)$ + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	2.70	0				*	(25)
	Disubstituted benzene													
	Aryl(diphenyl), Aryl-alkoxyl													
.395	1-$C_6H_5CH_2O$-4-$C_6H_5C_6H_4$ + Cl_2	Ac 99*	10^3A= 5; 10^3B= 2.5	HCl	0.01	*k* AB	20	9.05	-1				*	(25)
.396	1-$C_6H_5CH_2O$-4-(4'-$NO_2C_6H_4$)C_6H_4 + Cl_2	Ac 99*	10^3A= 5; 10^3B= 2.5	HCl	0.01	*k* AB	20	8.92	-2				*	(25)
.397	1-(4'-$NO_2C_6H_4CH_2O$)-4-$C_6H_5C_6H_4$ + Cl_2	Ac 99*	10^3A= 5; 10^3B= 2.5	HCl	0.01	*k* AB	20	1.73	-1				*	(25)
	Disubstituted diphenyl													
	Alkoxyl, Halogen													
.398	4-F-$C_6H_4C_6H_4$-4'-OCH_3 + Cl_2	Ac 99*	10^2A= 1; 10^3B= 5	HCl	0.02	*k* AB	20	7.90	-1				*	(25)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.399	$4\text{-Cl-}C_6H_4C_6H_4\text{-}4'\text{-}OCH_3 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	6.12	-1				*	(25)
.400	$4\text{-Br}C_6H_4C_6H_4\text{-}4'\text{-}OCH_3 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	5.70	-1				*	(25)
.401	$4\text{-F-}C_6H_4C_6H_4\text{-}4'\text{-}OC_2H_5 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.53	0				*	(25)
.402	$4\text{-Cl-}C_6H_4C_6H_4\text{-}4'\text{-}OC_2H_5 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.18	0				*	(25)
.403	$4\text{-Br-}C_6H_4C_6H_4\text{-}4'\text{-}OC_2H_5 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.09	0				*	(25)
.404	$4\text{-Cl-}C_6H_4C_6H_4\text{-}4'\text{-}OCH(CH_3)_2 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	2.47	0				*	(25)
	Heterocyclic substituted benzene													
.404.1	1,2-$\overline{CH_2CH_2OC_6H_4} + Br_2$ (coumaran)	Ac*	$10^2A = 1$; $10^3B = 1$			k AB	20	2.5	0					(1b)
.404.2	1,2-$\overline{CH_2CH_2CH_2OC_6H_4} + Br_2$ (chroman)	Ac*	$10^2A = 1$; $10^3B = 1$			k AB	20	9.9	-1					(1b)
.404.3	1,2-$\overline{CH_2CH_2CH_2CH_2OC_6H_4} + Br_2$ (homochroman)	Ac*	$10^2A = 1$; $10^3B = 1$			k AB	20	4.85	-2					(1b)
	Three substituents on Benzene Dialkyl, Hydroxyl													
.405	$1,2\text{-}(CH_3)_2\text{-}4\text{-}O\bar{C}_6H_3 + HOCl$	H_2O	$10^3A = 2\text{-}10$; $10^3B \simeq 1$	NaOH	0-0.01	k AB	25	3.37	+4				*	(34)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addendd	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.405.1	$1,3-(CH_3)_2-2-CH_3OC_6H_3 + Br_2$	Ac*	$10^2A = 1$; $10^3B = 1$			k AB	20	1.3	-2					([1b])
Three substituents on Benzene Dialkyl, Halogen														
.405.2	$1,4-(CH_3)_2-2-IC_6H_3 + ICl$	CF_3COOH	$10^2A = 4.7$; $10^3B = 4$ 2.3 4			k AB	25 25	3.2 3.7	-2 -2					([1a])
Three substituents on Benzene Alkyl, Hydroxyl, Halogen														
.406	$1-CH_3-4-O^-6-Cl-C_6H_3 + HOCl$	H_2O	$10^3A = 2-10$; $10^3B \simeq 1$	NaOH	0-0.01	k AB	25	2.78	+3				*	([34])
Three substituents on Benzene Alkoxyl, Carboxyl, Halogen														
.407	$1-CH_3O-2-COOCH_3-4-Cl-C_6H_3 + HOBr$	AcW 75*				k AB	20	2.56	-1					([14])
.408	$1-CH_3O-4-COOCH_3-6-Cl-C_6H_3 + HOBr$	AcW 75*				k AB	20	6.26	-2					([14])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.409	$1\text{-}CH_3O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	6.48	-2					([14])
.410	$1\text{-}C_2H_5O\text{-}4\text{-}COOCH_3\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.24	-1					([14])
.411	$1\text{-}C_2H_5O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.30	-1					([14])
.412	$1\text{-}CH_3CH_2CH_2O\text{-}4\text{-}COOCH_3\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.40	-1					([14])
.413	$1\text{-}CH_3CH_2CH_2O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.45	-1					([14])
.414	$1\text{-}(CH_3)_2CHO\text{-}2\text{-}COOCH_3\text{-}4\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	8.40	-1					([14])
.415	$1\text{-}(CH_3)_2CHO\text{-}4\text{-}COOCH_3\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	2.08	-1					([14])
.416	$1\text{-}(CH_3)_2CHO\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	2.24	-1					([14])
.417	$1\text{-}CH_3(CH_2)_3O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.53	-1					([14])
.418	$1\text{-}CH_3(CH_2)_4O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Cl\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.53	-1					([14])
.419	$1\text{-}CH_3O\text{-}2\text{-}COOCH_3\text{-}4\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	3.45	-1					([14])
.420	$1\text{-}CH_3O\text{-}4\text{-}COOCH_3\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	8.40	-2					([14])
.421	$1\text{-}CH_3O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	8.81	-2					([14])
.422	$1\text{-}C_2H_5O\text{-}2\text{-}COOCH_3\text{-}4\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	6.86	-1					([14])
.423	$1\text{-}C_2H_5O\text{-}4\text{-}COOCH_3\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.66	-1					([14])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.424	$1\text{-}C_2H_5O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.77	-1					(14)
.425	$1\text{-}CH_3CH_2CH_2O\text{-}4\text{-}COOCH_3\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.92	-1					(14)
.426	$1\text{-}CH_3CH_2CH_2O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	2.00	-1					(14)
.427	$1\text{-}(CH_3)_2CHO\text{-}2\text{-}COOCH_3\text{-}4\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	1.02	0					(14)
.428	$1\text{-}(CH_3)_2CHO\text{-}4\text{-}COOCH_3\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	3.05	-1					(14)
.429	$1\text{-}(CH_3)_2CHO\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	3.19	-1					(14)
.430	$1\text{-}CH_3(CH_2)_3O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	2.05	-1					(14)
.431	$1\text{-}CH_3(CH_2)_4O\text{-}4\text{-}COOC_2H_5\text{-}6\text{-}Br\text{-}C_6H_3 + HOBr$	AcW 75*				k AB	20	2.06	-1					(14)
	Three Substituents on Benzene													
	Alkyl, Aryl-alkoxyl, Halogen													
.432	$1\text{-}CH_3\text{-}2\text{-}C_6H_5CH_2O\text{-}5\text{-}Cl\text{-}C_6H_3 + Cl_2$	Ac 99*	$A = 3B \simeq 0.01$	HCl		k AB	20	3.88	-2				*	(24)
.433	$1\text{-}CH_3\text{-}2\text{-}(o\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Cl\text{-}C_6H_3 + Cl_2$	Ac 99*	$A = 3B \simeq 0.01$	HCl		k AB	20	6.03	-3				*	(24)
.434	$1\text{-}CH_3\text{-}2\text{-}(2',6'\text{-}Cl_2C_6H_4CH_2O)\text{-}5\text{-}Cl\text{-}C_6H_3 + Cl_2$	Ac 99*	$A = 3B \simeq 0.01$	HCl		k AB	20	1.43	-2				*	(24)
.435	$1\text{-}CH_3\text{-}4\text{-}C_6H_5CH_2O\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	$A = 3B \simeq 0.01$	HCl		k AB	20	6.65	-2				*	(24)
.436	$1\text{-}CH_3\text{-}2\text{-}(o\text{-}CH_3C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	$A = 3B \simeq 0.01$	HCl		k AB	20	5.48	-2				*	(24)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.437	$1\text{-}CH_3\text{-}4\text{-}(o\text{-}CH_3C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	7.63	-2				*	(24)
.438	$1\text{-}C_2H_5\text{-}4\text{-}(o\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	1.50	-2				*	(24)
.439	$1\text{-}C_2H_5\text{-}4\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	1.63	-2				*	(24)
.440	$1\text{-}CH_3CH_2CH_2\text{-}4\text{-}(o\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	1.08	-2				*	(24)
.441	$1\text{-}CH_3CH_2CH_2\text{-}4\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	1.23	-2				*	(24)
.442	$1\text{-}(CH_3)_3C\text{-}4\text{-}(o\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	5.60	-3				*	(24)
.443	$1\text{-}(CH_3)_3C\text{-}4\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	6.55	-3				*	(24)
.444	$1\text{-}(CH_3)_3C\text{-}4\text{-}(2',6'\text{-}Cl_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	1.16	-2				*	(24)
.445	$1\text{-}(CH_3)_2CH(CH_2)_2\text{-}4\text{-}C_6H_5CH_2O\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	2.63	-2				*	(24)
.446	$1\text{-}(CH_3)_2CH(CH_2)_2\text{-}4\text{-}(o\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	4.28	-3				*	(24)
.447	$1\text{-}(CH_3)_2CH(CH_2)_2\text{-}4\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}5\text{-}Br\text{-}C_6H_3 + Cl_2$	Ac 99*	A = 3B ≃ 0.01	HCl		k AB	20	5.55	-3				*	(24)
	Three Substituents on Benzene													
	Hydroxyl, Halogen, Halogen													
.448	$1\text{-}OH\text{-}2,4\text{-}Br_2\text{-}C_6H_3 + Br_2$	AcW 72*	$10^3A = 5$; $10^3B = 4$	$HClO_4$ LiBr	0.10 0.10	k AB	20	5.3	-1				*	(23)
		AcW 80*	7	$HClO_4$ LiBr	0.10 0.137		20	2.4	-1					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.449	1-OH-2,6-Br_2-C_6H_3 + Br_2	AcW80*	10^3A= 2.5; 10^3B= 4	HBr	0.30	*k* AB	20	1.60	-1				*	(23)
				"	0.20		20	2.44	-1					
				$HClO_4$	0.10									
				HBr	0.10		20	5.13	-1					
				$HClO_4$	0.20									
				HBr	0.20		20	1.99	-1					
				LiBr	0.10									
				HBr	0.10		20	3.02	-1					
				LiBr	0.20									
	Three Substituents on Benzene													
	Alkoxyl, Halogen, Halogen													
.450	1-CH_3O-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	2.83	-1					(14)
.451	1-C_2H_5O-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	5.66	-1					(14)
.452	1-$CH_3CH_2CH_2O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	6.34	-1					(14)
.453	1-$(CH_3)_2CHO$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	1.03	0					(14)
.454	1-$CH_3(CH_2)_3O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	6.45	-1					(14)
.455	1-$CH_3(CH_2)_4O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	6.52	-1					(14)
.456	1-$HOOCCH_2O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	2.30	-2					(14)
.457	1-$HOOC(CH_2)_2O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				*k* AB	20	1.36	-1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.458	1-HOOC(CH_3)CHO-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				k AB	20	2.74	-2					(14)
.459	1-HOOC(CH_3)CHO-2,6-Cl_2-C_6H_3 + HOBr	AcW75*				k AB	20	3	-3					(14)
.460	1-$C_6H_5CH_2O$-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				k AB	20	2.05	-1					(14)
.461	1-Br(CH_2)$_2$O-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				k AB	20	4.55	-2					(14)
.462	1-Br(CH_2)$_3$O-2,4-Cl_2-C_6H_3 + HOBr	AcW75*				k AB	20	1.60	-1					(14)
.463	1-CH_3O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	3.73	-1					(14)
.464	1-CH_3O-2,6-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	8	-3					(14)
.465	1-C_2H_5O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	7.47	-1					(14)
.466	1-$CH_3CH_2CH_2O$-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	8.52	-1					(14)
.467	1-(CH_3)$_2$CHO-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	1.36	0					(14)
.468	1-CH_3(CH_2)$_3$O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	8.60	-1					(14)
.469	1-(CH_3)$_2$CHCH_2O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	1.01	0					(14)
.470	1-CH_3(CH_2)$_4$O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	8.80	-1					(14)
.471	1-(CH_3)$_2$CH(CH_2)$_2$O-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	9.74	-1					(14)
.472	1-$C_6H_5CH_2O$-2,4-Br_2-C_6H_3 + HOBr	AcW75*				k AB	20	2.65	-1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Three Substituents on Diphenyl Alkoxyl, Halogen, Nitro													
.473	4'-NO_2-3-Cl-4-CH_3O-$C_6H_4C_6H_3$ + Cl_2	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	*k* AB	20	3.2	-4				*	(25)
.474	4'-NO_2-3-Cl-4-C_2H_5O-$C_6H_4C_6H_3$ + Cl_2	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	*k* AB	20	6.45	-4				*	(25)
.475	4'-NO_2-3-Cl-4-$CH_3CH_2CH_2O$-$C_6H_4C_6H_3$ + Cl_2	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	*k* AB	20	6.92	-4				*	(25)
.476	4'-NO_2-3-Cl-4-$(CH_3)_2CHO$-$C_6H_4C_6H_3$ + Cl_2	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	*k* AB	20	9.40	-4				*	(25)
	Four Substituents on Benzene Alkyl, Alkyl, Alkyl, Halogen													
								time	% reacted					
.477	1,3,5-$(CH_3)_3$-2-F-C_6H_2 + Br_2	CH_3NO_2	A = B = 0.01				30	1,700	10				*	(23a)
.478	1,3,5-$(CH_3)_3$-2-Cl-C_6H_2 + Br_2	CH_3NO_2	A = B = 0.01				30	2,920	10				*	(23a)
			0.02				30	720	10					
		AcNm*	0.01				30	9,000	10					
.479	1,3,5-$(CH_3)_3$-2-Br-C_6H_2 + Br_2	CH_3NO_2	A = B = 0.01				30	3,290	10				*	(23a)
		AcNm*	0.01				30	15,800	10					
.480	1,3,5-$(CH_3)_3$-2-I-C_6H_2 + Br_2	CH_3NO_2	A = B = 0.01				30	1,270	10				*	(23a)
	Four Substituents on Diphenyl													
.481	3,3'-Cl_2-4,4'-$(CH_3O)_2$-$(C_6H_3)_2$ + Cl_2	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	*k* AB	20	6.03	-3				*	(25)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.482	$3,3'\text{-}Cl_2\text{-}4,4'\text{-}(C_2H_5O)_2\text{-}(C_6H_3)_2 + Cl_2$	Ac 99*	$10^2A = 1$; $10^2B = 5$	HCl	0.02	k AB	20	1.19	-2				*	(25)
.483	$3,3'\text{-}Cl_2\text{-}4,4'\text{-}(n\text{-}C_3H_7O)_2\text{-}(C_6H_3)_2 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.29	-2				*	(25)
.484	$3,3'\text{-}Cl_2\text{-}4,4'\text{-}[(CH_3)_2CHO]_2\text{-}(C_6H_3)_2 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.63	-2				*	(25)
	Five Substituents on Benzene													
	Alkyl, Alkyl, Alkyl, Alkyl, Halogen													
								time	% reacted					
.485	$1,2,3,5\text{-}(CH_3)_4\text{-}4\text{-}F\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	870	10				*	(23a)
.486	$1,2,4,5\text{-}(CH_3)_4\text{-}3\text{-}F\text{-}C_6H + Br_2$	Ac*	A = B = 0.01				30	8,820	10				*	(23a)
			0.02				30	2,100	10					
.487	$1,2,3,5\text{-}(CH_3)_4\text{-}4\text{-}Cl\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	1,650	10				*	(23a)
.488	$1,2,4,5\text{-}(CH_3)_4\text{-}3\text{-}Cl\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	830	10				*	(23a)
		AcNm*	0.01				30	4,520	10					
.489	$1,2,3,5\text{-}(CH_3)_4\text{-}4\text{-}Br\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	1,690	10				*	(23a)
.490	$1,2,4,5\text{-}(CH_3)_4\text{-}3\text{-}Br\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	1,980	10				*	(23a)
			0.02				30	515	10					
		AcNm*	0.01				30	10,400	10					
.491	$1,2,3,5\text{-}(CH_3)_4\text{-}4\text{-}I\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	320	10				*	(23a)
.492	$1,2,4,5\text{-}(CH_3)_4\text{-}3\text{-}I\text{-}C_6H + Br_2$	CH_3NO_2	A = B = 0.01				30	1,500	10				*	(23a)

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Five Substituents on Benzene															
Alkoxyl, Alkyl, Alkyl, Nitro, Halogen															
.493		1-CH_3O-3,5-$(CH_3)_2$-2-NO_2-4-Cl-C_6H + HOBr	AcW75*				k AB	20	7.42	-1					(14)
.494		1-C_2H_5O-3,5-$(CH_3)_2$-2-NO_2-4-Cl-C_6H + HOBr	AcW75*				k AB	20	1.42	0					(14)
.495		1-$C_6H_5CH_2O$-3,5-$(CH_3)_2$-2-NO_2-4-Cl-C_6H + HOBr	AcW75*				k AB	20	4.93	-1					(14)
Five Substituents on Benzene															
Alkoxyl, Alkyl, Alkyl, Halogen, Halogen															
.496		1-$HOOCCH_2O$-3,5-$(CH_3)_2$-2,4-Cl_2- C_6H + HOBr	AcW75*				k AB	20	3.1	0					(14)
.497		1-(o-$CH_3C_6H_4CH_2O$)-3,5-$(CH_3)_2$-2,4-Cl_2-C_6H + Cl_2	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	1.72	-1				*	(24)
.498		1-(o-$NO_2C_6H_4CH_2O$)-3,5-$(CH_3)_2$-2,4-Cl_2-C_6H + Cl_2	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	2.05	-2				*	(24)
.499	.268	1-(o-$ClC_6H_4CH_2O$)-3,5-$(CH_3)_2$-2,4-Cl_2-C_6H + Cl_2	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	4.95	-2				* (23b) (24)	
Monosubstituted Napthalene															
Halogen															
									time	% reacted					
.500		1-$FC_{10}H_7$ + Cl_2 ⟶ (4)	Ac*	A = B = 0.025				25	150	20				*	(18)
.501		1-$FC_{10}H_7$ + Br_2 ⟶ (4)	Ac*	A = B = 0.10				25	2,240	10				*	(18)
				0.20				25	330	10					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
								time		% reacted				
.501	$1\text{-}FC_{10}H_7 + Br_2 \longrightarrow (4)$ *(continued)*	Ac*	A = B = 0.10	$HClO_4$	0.50		25	144		10			*	(18)
			0.20		0.50		25	30		10				
			0.05		0.50		52	284		10				
			0.10		0.50		52	60		10				
.502	$1\text{-}ClC_{10}H_7 + Cl_2 \longrightarrow (4)$	Ac*	A = B = 0.025				25	2,700		20			*	(18)
			0.20				25	276		20				
.503	$1\text{-}ClC_{10}H_7 + Br_2 \longrightarrow (4)$	Ac*	A = B = 0.10				25	70,200		10			*	(18)
			0.20				25	8,340		10				
			0.10	$HClO_4$	0.50		25	4,860		10				
			0.20		0.50		25	840		10				
			0.05		0.50		52	7,200		10				
			0.10		0.50		52	1,680		10				
		Ac 83*	0.05				25	6,600		10				
			0.10	$HClO_4$	0.169		25	1,290		10				
			0.20				25	210		10				
		Ac 51*	0.0062				52	960		20				
			0.0125				52	486		20				
.504	$1\text{-}BrC_{10}H_7 + Cl_2 \longrightarrow (4)$	Ac*	A = B = 0.025				25	3,240		20			*	(18)
.505	$1\text{-}BrC_{10}H_7 + Br_2 \longrightarrow (4)$	Ac*	A = B = 0.10				25	108,000		10			*	(18)
			0.20				25	13,320		10				
			0.10	$HClO_4$	0.50		25	7,320		10				
			0.20		0.50		25	1,320		10				
			0.05		0.50		52	8,880		10				
			0.10		0.50		52	2,160		10				

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
								time		% reacted				
.506	$1\text{-}IC_{10}H_7 + Br_2 \longrightarrow (4)$	Ac*	A = B = 0.10				25	37,200		10			*	(18)
			0.20				25	5,460		10				
			0.10	$HClO_4$	0.50		25	3,780		10				
			0.20		0.50		25	600		10				
			0.05		0.50		52	3,840		10				
			0.10		0.50		52	840		10				
	Disubstituted Napthalene													
	Alkoxyl, Nitro													
.507	$1\text{-}CH_3O\text{-}2\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.21	-2				*	(25)
.508	$1\text{-}CH_3O\text{-}4\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	7.08	-1				*	(25)
.509	$1\text{-}C_2H_5O\text{-}2\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.68	-2				*	(25)
.510	$1\text{-}C_2H_5O\text{-}4\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.25	0				*	(25)
.511	$1\text{-}CH_3CH_2CH_2O\text{-}4\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.20	0				*	(25)
.512	$1\text{-}C_6H_5CH_2O\text{-}4\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	4.20	-1				*	(25)
.513	$1\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}2\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.62	-3				*	(25)
.514	$1\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}4\text{-}NO_2\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.03	-1				*	(25)
	Disubstituted Napthalene													
	Alkoxyl, Halogen													
.515	$1\text{-}CH_3O\text{-}2\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	2.44	-1				*	(25)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.516	$1\text{-}C_2H_5O\text{-}2\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	3.81	-1				*	(25)
.517	$1\text{-}CH_3CH_2CH_2O\text{-}2\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	4.51	-1				*	(25)
.518	$1\text{-}C_6H_5CH_2O\text{-}2\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	1.79	-1				*	(25)
.519	$1\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}2\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	4.00	-2				*	(25)
.520	$1\text{-}(p\text{-}NO_2C_6H_4CH_2O)\text{-}4\text{-}Cl\text{-}C_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1$; $10^3B = 5$	HCl	0.02	k AB	20	~1.1	+1				*	(25)

CODED SOLVENTS

Ac*	CH_3COOH
Ac 85, (80)...*	CH_3COOH % designated + H_2O
DiW 50*	Dioxane 50 wt % + H_2O
AcC 90*	CH_3COOH + 10 vol % CCl_4
AcB 90*	CH_3COOH + 10 vol % C_6H_6
M 30, (25)...*	CH_3OH vol % designated + H_2O
Di 30*	Dioxane 30 vol % + H_2O
AcW 75* (10) (25) (50) (65) (85)	CH_3COOH weight % designated + H_2O
AcD*	Deuterium substituted CH_3COOH
AcD 90*	90 vol % deuterium substituted CH_3COOH + D_2O
AcNm*	CH_3COOH + CH_3NO_2 (1:1 by volume)

COMMENTS

(.272) - (.273)	Unsubstituted aromatic hydrocarbons
(.274) - (.300)	Alkyl substituted benzene
(.301) - (.317)	*Monosubstituted benzene*
(.301) - (.309)	Alkoxyl(hydroxyl) substituted benzene
(.310) - (.312)	Carboxyl substituted benzene
(.313) - (.315)	Amino(amide) substituted benzene
(.316) - (.317)	Sulfo-alkyl substituted benzene
(.318) - (.396)	*Disubstituted benzene*
(.318) - (.332)	Alkyl, Hydroxyl(alkoxyl)
(.333) - (.335)	Di-alkoxyl
(.336)	Alkoxyl, carboxyl
(.337) - (.340)	Alkyl, Amino
(.341) - (.347)	Hydroxyl, Nitro
(.348) - (.356)	Alkoxyl, Nitro
(.357)	Aryl alkoxyl, Nitro
(.358) - (.359)	Amino(amide), Nitro
(.360) - (.373)	Alkoxyl, Halogen
(.374) - (.380)	Arylalkoxyl, Halogen
(.381)	Amino, Halogen
(.382) - (.397)	Aryl(diphenyl), Alkoxyl
(.398) - (.404)	Disubstituted diphenyl-
	Alkoxyl, Halogen
(.405) - (.472)	Three Substituents on Benzene
(.405)	Alkyl, Alkyl, Hydroxyl
(.406)	Alkyl, Hydroxyl, Halogen
(.407) - (.431)	Alkoxyl, Carboxyl, Halogen
(.432) - (.447)	Alkyl, Arylalkoxyl, Halogen
(.448) - (.449)	Hydroxyl, Halogen, Halogen
(.450) - (.472)	Alkoxyl, Halogen, Halogen
(.473) - (.476)	Three Substituents on Diphenyl
	Alkoxyl, Halogen, Nitro
(.477) - (.480)	Four Substituents on Benzene
	Alkyl, Alkyl, Alkyl, Halogen
(.481) - (.484)	Four Substituents on Diphenyl
	Alkoxyl, Alkoxyl, Halogen, Halogen
(.485) - (.499)	Five Substituents on Benzene
(.485) - (.492)	Alkyl, Alkyl, Alkyl, Alkyl, Halogen
(.493) - (.495)	Alkoxyl, Alkyl, Alkyl, Nitro, Halogen
(.496) - (.499)	Alkoxyl, Alkyl, Alkyl, Halogen, Halogen
(.500) - (.506)	Monosubstituted Napthalene
(.500) - (.506)	Halogen
(.507) - (.520)	Disubstituted Napthalene
(.507) - (.514)	Alkoxyl, Nitro
(.515) - (.520)	Alkoxyl, Halogen

COMMENTS *(continued)*

Reaction. **(.272)** Rate law does not include dependence on $[ZnCl_2]$. HBr inhibits probably by complexing with $ZnCl_2$. Plot of $1/k$ vs. [HBr] is linear. **(.273)** Selected data, units, seconds converted from original minutes. **(.274)** Rate law of ([1]) does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear for $ZnCl_2$ catalyzed reaction. Attributed to the formation of an inactive $ZnCl_2 \cdot HBr$ complex. Time for 10% reaction given by ([5])([33]). Detailed study by ([36]) on dependence of rate upon $C_6H_5CH_2$, Br_2 and I_2 shows rate determining step may be expressed as first order with respect to $C_6H_5CH_3 \cdot HBr$ and third order with respect to IBr. **(.275)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to the formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.276)** Units, seconds converted from original minutes. **(.277)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to the formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.278)** **(.279)** Units, seconds converted from original minutes. **(.280)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.281)** **(.282)** **(.283)** **(.284)** **(.285)** **(.286)** Units, seconds converted from original minutes. **(.287)** **(.288)** **(.289)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.290)** Units, seconds converted from original minutes. **(.291)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.292)** Units, seconds converted from original minutes of ([19]). Rate law of ([1]) does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.293)** Selected data. Units, seconds converted from original minutes. Rate law holds up to 50% reaction. $k = k_o + k'[H^+] + k''[H^+]A$ over range studied $k_o = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$, $k'' = 0.193$. Values of k_o and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See (.301)(.305)(.322)(.323). **(.294)** Selected data of ([26])([28]). Units, seconds converted from original minutes of ([28]). Original units of ([26]) mixed, both seconds and minutes used. Rate law followed to 75% reaction. ([31]) gives rate dependence upon HBr but no rate constants. Selected data of ([27]) in

COMMENTS *(continued)*

CCl_4. Seconds converted from original minutes. Induction period if HBr not introduced initially. Rate law followed to 90% reaction. Pseudo first order with respect to B, one-half order with respect to HBr and zero order with respect to A since A in sufficient excess. Rate constant calculated by dividing pseudo 3/2 order constant by concentration of A. Reaction carried out in dark to avoid side chain bromination. Strong catalysis by impurities in commercial mesitylene. Selected data of ([10]) in CCl_4. ([32]) gives rate law in agreement with ([10]) and times for fractional reaction. **(.295) (.296) (.297)** Rate law does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to the formation of an inactive $ZnCl_2 \cdot HBr$ complex. **(.298) (.299)** Rate law of ([1]) does not include dependence on $[ZnCl_2]$. Plot of $1/k$ vs. [HBr] is linear, which is attributed to the formation of an inactive $ZnCl_2 \cdot HBr$ complex. ([19]) gives times for 10% reaction. **(.300)** Units, seconds converted from original minutes. Ratio of $(CH_3)_5C_6I$ to $(CH_3)_5C_6Cl$ estimated from amount of I_2 at infinite time. The HI formed on chlorination reacts with ICl to form unreactive I_2. **(.301)** Selected data of ([17]) units, seconds converted from original. Pseudo first order rate law followed up to 50% reaction. Pseudo first order constant expressed by ([17]) by the equation $k = k_o + k'[H^+] + k''[H^+]A$ with values $k_o = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 0.473$ in the range studied. Values of k_o and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See (.293) (.305) (.322) (.323). In presence of HCl rate constant observed by ([34]) had identical values for phenols and phenolic ethers studied at phenol concentrations greater than value listed. See (.305) (.308) (.320). Rate determining step may be $HCl + HOCl \longrightarrow Cl_2 + H_2O$. **(.302)** $C_6H_5O^-$ and HOCl considered to be reactive species by ([34]) rather than C_6H_5OH and OCl^- based on study of OH^- dependence of rate of chlorination of salicyclic acid. Units, seconds converted from original minutes. **(.303)** Units, seconds converted from original minutes. **(.304)** Selected data of ([3]), ([30]). Units, seconds converted from original minutes of ([3]), ([7]), ([30]). Rate law followed up to about 50% reaction by ([3]) and 60% reaction by ([7]). KI also added 0.1 M/l by ([30]), 0.12 by ([3]) and 0.03-0.12 by ([7]). Empirical expression for k developed by ([3]) at pH 5.7-6.6 an d 5.6-6.0 respectively: at 25° $k = 10^{-8} \times [H^+]^{-1}\{0.557 + 37.5[Na_2HPO_4] + 1[KH_2PO_4]\}$ at 35° $k = 10^{-8}[H^+]^{-1}\{2.22 + 153[Na_2HPO_4] + 9.0[KH_2PO_4]\}$.

COMMENTS *(continued)*

Phenoxide ion considered to be reacting species and rate constant also calculated in terms of it. **(.305)** Ag^+ introduced by ([15]), ([16]) and ([17]) to keep Cl^- concentration low. ([15]) observes rate to be identical to rate for $C_6H_4(OCH_3)_2$ and C_6H_5OH. See (.301) and (.334). Selected data of ([17]). Units, seconds converted from original minutes. Rate constant expressed by ([17]) by the equation $k = k_o + k'[H^+] + k''[H^+]A$ with values $k_o = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 0.109$ in the range studied. Values of k_o and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See (.293) (.301) (.322) (.323). In presence of HCl rate constant observed by ([34]) had identical values for phenols and phenolic ethers studied at phenol or ether concentrations greater than value listed. See (.301) (.308) (.320). **(.306) (.307)** Units, seconds converted from original minutes. **(.308)** Units, seconds converted from original minutes. Rate constant identical to value observed by author for phenols and phenolic ethers studied in presence of HCl at phenol or ether concentration greater than value listed. See (.301) (.305) (.320). **(.309) (.311) (.312)** Units, seconds converted from original minutes. **(.313)** Pseudo second order rate law valid only under specified conditions as rate dependent upon [KI] and buffer constituents. From pH 5.4 to 7.6 k_o is independent of pH. Below pH 5.4 calculated value of k_o (extrapolated to zero buffer concentration) falls to 9.8×10^{-4} at pH = 4.57. Units, seconds converted from original minutes. Rate law followed to about 50% reaction. **(.314)** HI formed on chlorination reacts rapidly with ICl to form I_2 which is unreactive at stated conditions. Units, seconds converted from original minutes. **(.315)** Units, seconds converted from original minutes. **(.318) (.319)** Units, seconds converted from original minutes. Mechanism considered to involves ArO^- and HOCl see (.302). **(.320)** Units, seconds converted from original minutes. In presence of HCl and sufficient phenol rate identical for phenols and phenolic ethers studied by ([34]). See (.301) (.305) (.308). **(.321)** Rate law followed up to about 60% reaction. Units, seconds converted from original minutes. **(.322)** Rate law followed up to 50% reaction. Units, seconds converted from original minutes. Pseudo first order constant expressed by the equation $k = k_o + k'[H^+] + k''[H^+]A$ with values $k_o = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 1.30$ in the range studied. Values of k_o and k' identical for mesitylene, phenol, anisole and *m*- and *p*-tolyl methyl ether. See (.293) (.301)

COMMENTS *(continued)*

(.305) (.323). **(.323)** Units, seconds converted from original minutes. Pseudo first order constant expressed by ([17]) by the equation $k = k_o + k'[H^+] + k''[H^+]A$ with values $k_o = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 9 \times 10^{-2}$ in the range studied. Values of k_o and k' identical for mesitylene, phenol, anisole and *m*- and *p*-tolyl methyl ether. See (.293) (.301) (.305) (.322). ([35]) compares rate in deuterium substituted solvent see (.324). **(.324)** Units, seconds converted from original minutes. Since rate in D_2O is faster than in H_2O a rate controlling step is considered to be fission of $H_2OCl^+ \longrightarrow Cl^+ + H_2O$. **(.325)** HI formed in chlorination reacts with ICl to form I_2 which is unreactive at stated conditions. Percent of chlorination was estimated from iodine left at infinite time. Units, seconds converted from original minutes. **(.326) (.327) (.328)** Rate law followed to about 60% reaction. Units, seconds converted from original minutes. **(.329)** Calculated rate constants drift upward after 40% reaction. Units, seconds converted from original minutes. **(.330) (.331) (.332)** Rate law followed to about 60% reaction. Units, seconds converted from original minutes. **(.333)** Units, seconds converted from original minutes. **(.334)** Rate observed to be identical to rate for C_6H_5OH, and $C_6H_5OCH_3$, see (.301) (.305). **(.335)** Units, seconds converted from original minutes. **(.336)** Authors observe that plot of calculated k vs. $[Br^-][H^+]$ is linear. They suggest rate equation of the form $-dB/dt = k_1AB + k_2A[Br_2]$ and using the equilibrium constant for the reaction $Br_2 + H_2O = HOBr + Br^- + H^+$ calculate $k_1 = 0.108$ and $k_2 = 119$. **(.337) (.338) (.339) (.340)** Units, seconds converted from original minutes. Rate constants valid only under conditions specified. **(.341) (.342)** Units, seconds converted from original minutes. **(.343) (.344)** Simultaneous reactions. Units, seconds converted from original minutes, and M/l converted from original equivalents per liter. **(.345) (.346) (.347)** Units, seconds converted from original minutes. **(.348)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.349)** Rate law followed to 80% reaction and shown to be valid over two-fold variation in initial concentrations of A and B. Values of concentrations not stated. **(.350) (.352)** Cl_2 produced in reaction media from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.357)** Ring in which substitution occurs not specified. **(.358) (.359)** Units, seconds converted from

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COMMENTS *(continued)*

original minutes. **(.361) (.362) (.363) (.364) (.365) (.369) (.370) (.371)** Rate law in terms of free Br_2 as calculated using equilibrium constant for dissociation of Br_3^-. Units, seconds converted from original minutes. **(.374) (.376) (.379) (.380)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.381)** Rate law followed up to 65% reaction. Plot of rate constant vs. $[H^+]^{-1}$ is linear. Rate proportional to $K_1/(K_1 + [Cl^-])[Cl^-]$ where K_1 is equilibrium constant for $ICl_2^- \rightleftarrows ICl + Cl^-$. Rate constant corrected for change of volume with temperature. **(.382) through (.404)** Position of substitution not specified by ([25]). Classification based upon ring in which substitution thought to occur, (written last). Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.405) (.406)** Rate law in terms of phenolate ion and HOCl which authors consider to be involved in rate controlling step. Units, seconds converted from original minutes. **(.432) through (.447)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.448) (.449)** In absence of initial Br^- rate constant decreases with progress of reaction due to inhibition by Br^- formed. In reaction (.448) rate constant may be expressed by equation $k[Br_2][H^+]/(Br_2) = (3.2[H^+] + 0.63)/(0.26[Br^-] + 1.32[H^+][Br^-])$, where $[Br_2]$ represents total Br_2, and (Br_2) represents only free Br_2. **(.473) (.474) (.475) (.476)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.477) (.478) (.479) (.480)** Units, seconds converted from original minutes. (Relative rates to parent hydrocarbons also given). **(.481) (.482) (.483) (.484)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. **(.485) through (.492)** Units, seconds converted from original minutes. (Relative rates to parent hydrocarbons also given.) **(.497) (.498) (.499)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes. Rate constant for (.499) replaces the value listed in 1951 Tables which should have been 5.3×10^{-2} not 2.35×10^{-1}. **(.500) through (.506)** Units, seconds converted from original minutes. **(.507) through (.520)** Cl_2 produced in reaction medium from p-$CH_3C_6H_4SO_2NCl_2$. Units, seconds converted from original minutes.

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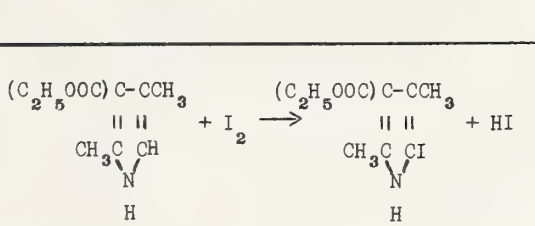
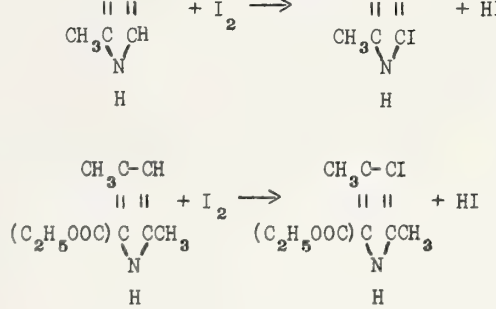
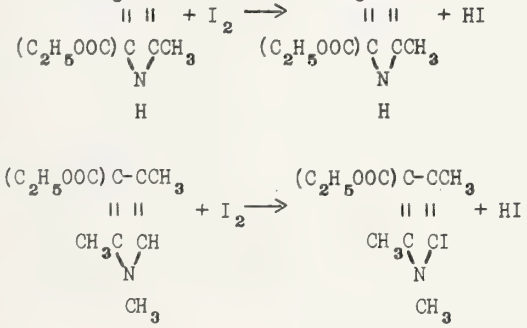
EXCHANGE

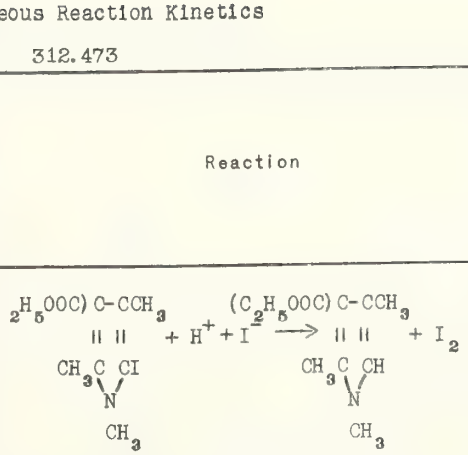
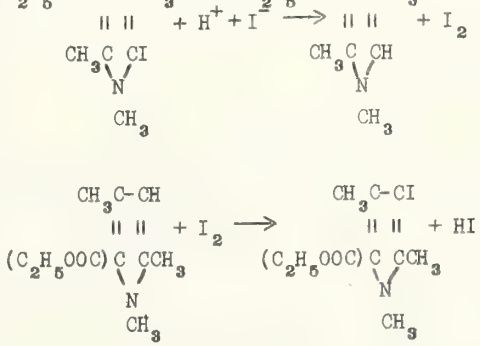
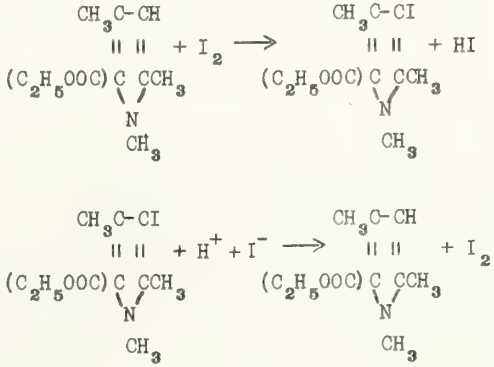
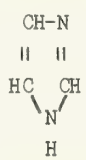
H replacement by halogen on heterocyclic ring

Reaction type: $RH + I_2 \longrightarrow RI + HI$
(A) (B) (L) (M)

Rate measured: $-dB/dt$

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	Comments	Literature
.1		H_2O + 28 wt% dioxane	10^3A = 5-6; 10^3B = 7-9	KI	0.5-0.8	$\frac{k\,AB}{1 + K[I^-]}$	26	1.57	+1	710	*	(1)
.2		H_2O + 28 wt% dioxane	10^3A = 5-6; 10^3B = 6-9	KI	0.6-0.9	$\frac{k\,AB}{1 + K[I^-]}$	26	6.0	-1	710	*	(1)
.3		H_2O + 28 wt% dioxane	$10^3A \sim 9$; $10^3B \sim 6$	KI	0.5-0.8	$\frac{k\,AB}{1 + K[I^-]}$	26	1.7	+1	710	*	(1)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	K	Comments	Literature
.3.		H_2O + 28 wt % dioxane		HCl KI	 0.5-0.8	k ABC	26	1.40	-2		*	([1])
.4		H_2O + 28 wt % dioxane	$10^3A \sim 6$; 10^3B = 6-8	KI	0.5-0.6	$\frac{k\,AB}{1 + K[I^-]}$	26	6.9	-1	710	*	([1])
.4.1		H_2O + 28 wt % dioxane		HCl KI	 0.5-0.6	k ABC	26	6.9	-4		*	([1])
.5	 + $2I_2 \longrightarrow C_3H_2N_2I_2 + 2HI$	H_2O	10^2A = 1.5-8; 10^4B = 4-5 μ = 0.05	$HClO_4$ KI $10^8[H^+]$ =	0.007-0.02 0.007-0.02 3-20	$-2dA/dt =$ $k\,AB[H^+]^{-1}[I^-]^{-2} +$ $k'A^2B[H^+]^{-1}[I^-]^{-2}$	25 k = k' =	 1.10 8.9	 -13 -12		*	([2])

COMMENTS

Reaction. **(.1) (.2) (.3)** In buffered solution pH = 6.8 to 6.9. Reverses in presence of strong acid. **(.3.1)** Reverse of reaction (.3) in presence of acid. **(.4)** In buffered solution pH = 6.8-6.9. **(.4.1)** Reverse of (.4) in presence of acid. **(.5)** Observed rate pseudo first order as A and I^- both in large excess. Calculated values of k and k' based upon free glyoxaline for A (total glyoxaline minus perchloric acid), stoichiometric I_2 assumed to be predominantly I_3^-. Authors consider reactive form to be either I^+ or H_2OI^+. Rate determining step probably replacement of first hydrogen since monoiodide reacts very much more rapidly even though A in twenty fold excess.

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EXCHANGE

Replacement of H by halogen on Si

Reaction types: $RR'R''SiH + X_2 \longrightarrow RR'R''SiX + HX$

and $RR'R''SiH + AgClO_4 \longrightarrow RR'R''SiClO_4 + Ag + \frac{1}{2}H_2$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$(C_2H_5)_3SiH + I_2 \longrightarrow (C_2H_5)_3SiI + HI$	CCl_4	$10^3A = 5-33$; $10^3B = 5-33$	$k\,AB^3$	-18	1.28	0	*	([1])
					-9	1.20	0		
					1	1.36	0		
					10	1.78	0		
					25	3.14	0		
		C_6H_6			25	7.7	+1		
		$CHCl_3$			25	5.9	+2		
.2	$(C_2H_5)_3SiH + AgClO_4 \longrightarrow (C_2H_5)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$10^2A = 5-26$; $B = 0.17-0.36$	k_oAB^2	23	1.2	-2	*	([2])
			$B = 0.4$		23	1.6	-2		
		C_6H_6	$10A = 1.1$; $10B = 1.2-1.7$		23	2.2	-2		
.3	$(n\text{-}C_3H_7)_3SiH + I_2 \longrightarrow (n\text{-}C_3H_7)_3SiI + HI$	CCl_4	$A = B = 0.01-0.05$	$k\,AB^3$	25	3.0	0	*	([1])
		C_6H_6			25	1.77	+1		
.4	$(n\text{-}C_3H_7)_3SiH + AgClO_4 \longrightarrow (n\text{-}C_3H_7)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14$; $B = 0.31$	k_oAB^2	23	6.3	-3	*	([2])
.5	$[(CH_3)_2CH]_3SiH + I_2 \longrightarrow [(CH_3)_2CH]_3SiI + HI$	C_6H_6	$A = B = 0.01-0.05$	$k\,AB^3$	25	4.0	0	*	([1])

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.6	$[(CH_3)_2CH]_3SiH + AgClO_4 \longrightarrow [(CH_3)_2CH]_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.43	k_oAB^2	23	1.2	-5	*	(2)
.7	$(n\text{-}C_4H_9)_3SiH + I_2 \longrightarrow (n\text{-}C_4H_9)_3SiI + HI$	CCl_4 C_6H_6 $CHCl_3$	A = B = 0.01-0.05	kAB^3	25 25 25	5.0 2.09 1.66	0 +1 +3	*	(1)
.8	$(n\text{-}C_4H_9)_3SiH + AgClO_4 \longrightarrow (n\text{-}C_4H_9)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.31 0.43	k_oAB^2	23 23	4.7 5.2	-3 -3	*	(2)
.9	$[(CH_3)_2CHCH_2]_3SiH + I_2 \longrightarrow [(CH_3)_2CHCH_2]_3SiI + HI$	CCl_4 C_6H_6	A = B = 0.01-0.05	kAB^3	25 25	3.9 9.5	-1 -1	*	(1)
.10	$[(CH_3)_2CHCH_2]_3SiH + AgClO_4 \longrightarrow [(CH_3)_2CHCH_2]_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.43	k_oAB^2	23	1.8	-4	*	(2)
.11	$(C_6H_5CH_2)_3SiH + AgClO_4 \longrightarrow (C_6H_5CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.08; B = 0.06	k_oAB^2	23	~2.6	0	*	(2)
.12	$(p\text{-}CH_3C_6H_4CH_2)_3SiH + AgClO_4 \longrightarrow (p\text{-}CH_3C_6H_4CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.08; B = 0.06	k_oAB^2	23	~4.4	0	*	(2)
.13	$(p\text{-}ClC_6H_4CH_2)_3SiH + AgClO_4 \longrightarrow (p\text{-}ClC_6H_4CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.08; B = 0.06	k_oAB^2	23	9.2	-2	*	(2)
	Aryl-silanes								
.14	$C_6H_5(CH_3)_2SiH + AgClO_4 \longrightarrow C_6H_5(CH_3)_2SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.21 0.08 0.06	k_oAB^2	23 23	1.1 4.9	-1 -1	*	(2)
.15	$p\text{-}CH_3C_6H_4(CH_3)_2SiH + AgClO_4 \longrightarrow p\text{-}CH_3C_6H_4(CH_3)_2SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.08; B = 0.06	k_oAB^2	23	5.7	-1	*	(2)

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.16	$(C_6H_5)_3SiH + Br_2 \longrightarrow (C_6H_5)_3SiBr + HBr$	CCl_4	A = B = 0.025	time		% B remaining			
				60	18	60			([1])
				120	18	46			
				7×10^3	25	33			
				2×10^5	25	33			
.17	$(C_6H_5)_3SiH + I_2 \longrightarrow (C_6H_5)_3SiI + HI$	CCl_4	A = B = 0.01-0.05	$k\,AB^3$	25	3	-2	*	([1])
		$CHCl_3$				6.1	0		
.18	$(C_6H_5)_3SiH + AgClO_4 \longrightarrow (C_6H_5)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.43	$k_o AB^2$	23	5.8	-4	*	([2])
.19	$(p\text{-}CH_3C_6H_4)_3SiH + I_2 \longrightarrow (p\text{-}CH_3C_6H_4)_3SiI + HI$	CCl_4	A = B = 0.01-0.05	$k\,AB^3$	25	1.4	-1	*	([2])
.20	$(p\text{-}CH_3C_6H_4)_3SiH + AgClO_4 \longrightarrow (p\text{-}CH_3C_6H_4)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.43	$k_o AB^2$	23	2.2	-3	*	([2])
.21	$(p\text{-}ClC_6H_4)_3SiH + I_2 \longrightarrow (p\text{-}ClC_6H_4)_3SiI + HI$	$CHCl_3$	A = B = 0.01-0.05	$k\,AB^3$	25	1.1	-1	*	([1])
.22	$(p\text{-}ClC_6H_4)_3SiH + AgClO_4 \longrightarrow (p\text{-}ClC_6H_4)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	A = 0.14; B = 0.43	$k_o AB^2$	23	1.1	-4	*	([2])

COMMENTS

Reactions. **(.1)** Good fourth order rate constants observed over course of reaction and with ratio of A/B varied from 0.5-2. At 55° mixed third and fourth order observed. No effect on rate constant of light, O_2 or H_2O. Light does influence reaction products. **(.2)** Initial rate only. Over the course reaction appears to be slightly less than third order. Rate of hydrogen evolution followed, which was reproducible, although stoichiometry of reaction not always reproducible. Above 0.35 M/l B initial rate appears to be higher than second order with respect to B. **(.3)** Reaction order assumed identical to (.1). **(.4)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve.

COMMENTS *(continued)*

(.5) Reaction order assumed identical to (.1). **(.6)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. **(.7)** Reaction order assumed identical to (.1). **(.8)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. **(.9)** Reaction order assumed identical to (.1). **(.10) (.11) (.12) (.13) (.14) (.15)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. **(.17)** Reaction order assumed identical to (.1). **(.18)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. **(.19)** Reaction order assumed identical to (.1). **(.20)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. **(.21)** Reaction order assumed identical to (.1). **(.22)** Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve.

LITERATURE

([1]) D.R. Deans, C. Eaborn, *CSL* **1954**, 3169. ([2]) C. Eaborn, *CSL* **1955**, 2517.

EXCHANGE

Hydrogen by halogen on NH_3 and amine

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	μ	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments
.1	$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$	H_2O	$10^5A = 2.3$; $10^5B = 1.1$	~.0001	4.58	kAB	6	2.05	+1				*
				"	11.7	Observed constants in terms of total analytical concentrations	6	8.5	+1				
				"	4.58		15	4.8	+1				
				"	11.7		17	1.60	+2				
				"	4.58		25	1.27	+2				
				.0001	4.71		25	2.17	+2				
				.0001	6.11		25	3.67	+3				
				.0001	6.49		25	9.67	+3				
				.0011	10.95		25	1.53	+3				
				.012	12.05		25	1.23	+2				
				.015	12.23		25	9.7	+1				
				.021	12.30		25	6.2	+1				
				~.0001	11.70		31	3.07	+2				
				"	11.70		35	4.70	+2	11.0			
				"	4.58		37	3.53	+2	16.5			
					4.58	$k_sA'B'$	6	4.2	+6				
					11.70		6	4.7	+6				
					4.58		15	5.0	+6				
					11.70		17	5.3	+6				
					4.58		25	5.8	+6				
					11.70		31	6.0	+6				
					11.70		35	6.5	+6				
					4.58		37	7.2	+6	2.5	2.5	10	

No.	Reaction	Solvent	Amount of reactant	μ	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments
.2	$CH_3NH_2 + HOCl \longrightarrow CH_3NHCl + H_2O$	H_2O	$10^5A=2.3$; $10^5B=1.1$	$[OH^-]$ = 0.12		kAB	6.5	2.53	+2				*
				"	"		12	3.74	+2				
				"	"		16	4.91	+2				
				"	"		21	8.00	+2				
				"	"		25	1.11	+3	13.8			
				.0001	4.33		25	2.52	+2				
				.0001	4.87		25	8.83	+2				
				.0001	5.81		25	7.37	+3				
				.026	12.42		25	3.10	+3				
				.046	12.67		25	1.90	+3				
				.081	12.88		25	1.07	+3				
				$[OH^-]$ = 0.12		k_sA′B′	6.5	3.0	+8				
				"	"		16	3.8	+8				
				"	"		25	5.0	+8	4.5	6	13	
.3	$(CH_3)_2NH + HOCl \longrightarrow (CH_3)_2NCl + H_2O$	H_2O	$10^5A=2.3$; $10^5B=1.1$	$[OH^-]$ = 0.12		kAB	6	3.56	+2				*
				"	"		11	4.64	+2				
				"	"		14	5.42	+2				
				"	"		21	8.64	+2				
				"	"		25	1.05	+3	10			
				.0001	4.09		25	8.7	+1				
				.0001	4.97		25	8.35	+2				
				.0001	5.60		25	3.50	+3				
				.030	12.45		25	2.54	+3				
				.056	12.74		25	1.37	+3				
				.076	12.87		25	1.08	+3				
				$[OH^-]$ = 0.12		k_sA′B′	6	4.3	+8				
				"	"		14	4.7	+8				
				"	"		25	5.0	+8	0.8	1	11	

Supplement 1958

COMMENTS

Tabulated values of k are for observed second order rate law in terms of total concentrations of reactants. Specific second order rate constants in terms of calculated concentrations, A', B', of the specific chemical species are listed as k_s. The pH dependence is consistent with a reaction mechanism involving NH_3 with HOCl or NH_4^+ with OCl^-.

LITERATURE

I. Weil, J.C. Morris, *ACS* 1949, **71**, 1664.

EXCHANGE
HYDROGEN SUBSTITUTION
Replacement of hydrogen by halogen on nitrogen

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $RC{:}ONHR' + HOX \longrightarrow RC{:}ONXR' + H_2O$

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1) (Buffer acid)	Amount of addend (1)	Addend (2) (Buffer salt)	Amount of addend (2)	Defined mass action law	pH	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$CH_3C{:}ONHCH_3 + HOCl \longrightarrow CH_3C{:}ONClCH_3 + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	CH_3COOH	0.015	CH_3COONa	0.035	k AB	5.0	25	7.87	-3
					0.040		0.093		5.0	25	1.92	-2
					0.080		0.187		5.0	25	3.58	-2
					0.120		0.280		5.0	25	5.64	-2
					0.0038		0.096		6.0	25	3.22	-3
					0.0075		0.192		6.0	25	5.02	-3
					0.0150		0.385		6.0	25	8.35	-3
				(X)				$k = k_o + k_x[X]$				
				CH_3COOH	0.01-0.1	"	0.04-0.3		5.0	25	k_o 8	-4
					0.004-0.01		0.1-0.4		6.0	25	k_o 1.42	-3
									5-6	25	k_x 4.5	-1
				$CH_2ClCOOH$						25	k_x 2.50	0
				C_6H_5COOH						25	k_x 1.03	0
				o-$NO_2C_6H_4COOH$						25	k_x 7.33	0
				$(CH_2COOH)_2$						25	k_x 1.02	0
				$HOOC(CH_2)_2COO^-$						25	k_x 3.5	-1
				$H_2PO_4^-$	—	$HPO_4^=$	—		6	25	k_o 1.2	-3
					0.022		0.0028		6	25	1.85	-3
					0.044		0.0057		6	25	2.53	-3
					0.089		0.0114		6	25	3.85	-3
					—		—		7	25	k_o 5.2	-3
					0.010		0.015		7	25	5.50	-3

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1) (Buffer acid)	Amount of addend (1)	Addend (2) (Buffer salt)	Amount of addend (2)	Defined mass action law	pH	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$CH_3C{:}ONHCH_3 + HOCl \longrightarrow$ *(continued)*	H_2O	$10^2A = 2$; $10^3B = 5$	$H_2PO_4^-$	0.020	$HPO_4^=$	0.030	k AB	7	25	5.72	-3
					0.041		0.059		7	25	6.37	-3
									8	25	k_o 1.20	-2
				0.0016			0.0234		8	25	1.23	-2
				0.0032			0.0468		8	25	1.23	-2
				0.0064			0.0936		8	25	1.29	-2
							0.100		9	25	1.60	-2
.2	$CH_3C{:}ONHCH_2COOH + HOCl \longrightarrow CH_3C{:}ONClCH_2COOH + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	CH_3COOH	0.0038	CH_3COONa	0.096	k AB	6	25	5.93	-3
					0.0075		0.192		6	25	6.45	-3
					0.0150		0.385		6	25	7.70	-3
				$H_2PO_4^-$	0.044	$HPO_4^=$	0.0057		6	25	4.67	-3
.3	$CH_3C{:}ONHC_6H_4\text{-}o\text{-}CH_3 + HOCl \longrightarrow$ $CH_3C{:}ONClC_6H_4\text{-}o\text{-}CH_3 + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	CH_3COOH	0.0038	CH_3COONa	0.096	k AB	6	25	2.17	-1
					0.0075		0.192		6	25	2.08	-1
.4	$CH_3C{:}ONHC_6H_4\text{-}p\text{-}CH_3 + HOCl \longrightarrow$ $CH_3C{:}ONClC_6H_4\text{-}p\text{-}CH_3 + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	CH_3COOH	0.0075		0.192	k AB	6	25	1.80	-1
					0.0150		0.385		6	25	1.83	-1
				$H_2PO_4^-$	0.044	$HPO_4^=$	0.0057		6	25	1.80	-1
.5	$CH_3C{:}ONHC_6H_5 + HOCl \longrightarrow CH_3C{:}ONClC_6H_5 + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	$H_2PO_4^-$	0.015	$HPO_4^=$	0.035	k AB	5	25	2.28	-2
					0.044		0.0057		6	25	2.20	-1
					0.089		0.0114		6	25	1.88	-1
					0.020		0.030		7	25	1.65	0
					0.0032		0.0468		8	25	4.48	0
.6	$CH_3C{:}ONHCH_2C_6H_4\text{-}o\text{-}Cl + HOCl \longrightarrow$ $CH_3C{:}ONClC_6H_4\text{-}o\text{-}Cl + H_2O$	H_2O	$10^2A = 2$; $10^3B = 5$	CH_3COOH	0.0038	CH_3COONa	0.096	k AB	6	25	2.58	0
					0.0075		0.192		6	25	2.48	0
					0.0150		0.385		6	25	2.47	0
				$H_2PO_4^-$	0.044	$HPO_4^=$	0.0057		6	25	2.42	0

Supplement 1956

COMMENTS

Selected data. Units, seconds converted from original minutes. Rate law followed to about 65% reaction.

LITERATURE

R.P. Mauger, F.G. Soper, *CSL* **1946**, 71.

EXCHANGE

Replacement of halogen by NH_2 and :NH

Gas phase

Reaction type: $CX_4 + 7NH_3 \longrightarrow 4NH_4X + H_2NC(=NH)NH_2$

(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Time	% M formed	$k = k^o \times 10^n$ k^o	n	Comments
.1	$CCl_4 + NH_3$	A = 1.3; B ~ 10				150	6.5×10^4	0			*
			I_2	0.05		150	6.5×10^4	~ 10			
					k AL	300	6.5×10^4	10	5.3	-4	
			KI	1.3		300	6.5×10^4	84			
.2	$CBr_4 + NH_3$	A = 0.2; B ~ 10				150	6.5×10^4	62			*
			L	0.25		150	6.5×10^4	83			

COMMENTS

For these reactions below critical temperature of NH_3 see 332.753. Data gives order of magnitude only. Concentrations estimated at reaction temperatures. Reactions proceed through intermediate which involves about 10% of the reacting carbon for (.2) and less than 5% for (.1). Production of halide ion slightly ahead of guanidine at all stages.

LITERATURE

G. W. Watt, H. T. Hahn, *ACS* 1955, 77, 312.

EXCHANGE

Alkali metal replaced by C

Reaction type: $R_1COOR_2 + CH_2MCOR_3 \longrightarrow R_1COCH_2COR_3 + R_2OM$

followed by rapid $R_1COCH_2COR_3 + CH_2MCOR_3 \longrightarrow R_1COCHMCOR_3 + CH_3COR_3$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Literature and comments are at end of table.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	$\Delta S^{\ddagger}$	Comments
.1	$CH_3COOC_2H_5 + 2CH_2NaCOCH_2CH_2CH_3$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	0	7.7	-5					
					30	1.10	-3	14.5	3	7	-26.4	
.2	$CH_3COOC_2H_5 + 2CH_2NaCOCH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	0	9.4	-5					
					30	1.09	-3	13.8	1	7	-29.2	
.3	$CH_3COOC_2H_5 + 2CH_2LiCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	30	1.44	-3					
.4	$CH_3COOC_2H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	0	3.85	-4					
					30	5.25	-3	14.1	8	7	-24.4	
.5	$CH_3COOC_2H_5 + 2CH_2NaCOC(CH_3)_3$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	0	3.57	-5					
					30	4.03	-4	13.2	1	6	-33.1	
.6	$CH_3COOC_2H_5 + 2CH_2NaCOC_6H_5$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	0	2.60	-5					*
					30	3.52	-4	14.2	6	6	-29.5	
.7	$CH_3COOC_2H_5 + 2CH_2NaCOC_6H_2$-2,4,6-$(CH_3)_3$	$(C_2H_5)_2O$	10^2A=4-9; 10B= 1-2	$-dA/dt = kAB$	30	very slow						*

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	$\Delta S^{\ddagger}$	Comments
.8	$CH_3COOCH(CH_3)_2 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	0	1.80	-5					
					30	7.8	-4	20.6	6	11	-7.4	
.9	$CH_3COOC(CH_3)_3 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	30	very slow						*
.10	$(CH_3)_2CHCOOC_2H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	30	2.52	-4					
.11	$(CH_3)_2CHCH_2COOC_2H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	30	1.53	-4					
.12	$CH_3COOC_6H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	30	2.3	-1					*
.13	$C_6H_5COOC_2H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	0	1.07	-4					
					30	2.60	-3	17.5	1	10	-15.2	
.14	$C_6H_5COOC_6H_5 + 2CH_2NaCOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	10^2A=4-9; 10B=1-2	$-dA/dt = kAB$	0	7.2	-2					*
					30	2.2	-1	6	~	4	-43	

COMMENTS

General: Reactions studied in presence of excess of alkali metal ketone which was produced by titration with triphenyl methyl sodium or lithium. Diketone first produced reacts rapidly with second molecule of alkali metal ketone to produce sodium, or lithium, diketone so that differential rate equation has the form $dx/dt = k(a-x)(b-2x)$. "a" and "b" are initial concentrations of ester and alkali metal ketone and x is ester reacted at time t. Specific concentrations of reactants not stated in each case. When ester concentration was 0.20 and concentration of sodium ketone only 0.24 the above rate law did not hold. For all data listed concentration of B is greater than twice concentration of A. Authors give units of $\Delta S^{\ddagger}$ as k cals/deg. the units should be cals/deg. Values of E and ΔS are based on measurement at only two temperatures so that number after the decimal probably has no significance.

Reaction: **(.6)** Activation energy and $\Delta S^{\ddagger}$ recalculated as values given by authors do not agree with the data. **(.7)** **(.9)** No data given to indicate limiting value of rate constant. **(.12)** **(.14)** Value of rate constant in doubt as reaction too fast to measure accurately.

LITERATURE

D.G. Hill, J. Burkus, C.R. Hauser, *ACS* 1959, **81**, 602.

EXCHANGE

Replacement of B by O on aromatic C

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_5B(OH)_2 + H_2O_2 \longrightarrow C_6H_5OH + B(OH)_3$	H_2O	10^2A = 1-5 10^3B = 5-40	$HClO_4$	0.0025-0.01			k AB	25	7.7	-4	*	(1)
					0.20				25	1.56	-3		
					2.5				25	1.60	-2		
					8.2				25	6.05	-1		
					0.2-8		$k = k_o + k' a_{H_2O}^{-1} \cdot a_{HClO_4}^{-1}$		25	k_o 7.7	-4		
									25	k' 3.8	-3		
				H_2SO_4	0.193			k AB	25	1.84	-3		
					1.13				25	9.89	-3		
					3.64				25	9.19	-2		
					6.38				25	5.91	-1		
					8.99				25	3.6	0		
					0.2-9		$k = k_o + k' a_{H_2O}^{-\frac{1}{2}} \cdot a_{H_2SO_4}^{-3/2}$		25	k_o 7.7	-4		
									25	k' 1.4	-1		
				H_3PO_4	0.725			k AB	25	3.32	-3		
					2.27				25	1.40	-2		
					5.19				25	1.21	-1		
					9.67				25	2.14	0		
					0.7-9		$k = k_o + k' a_{H_2O} \cdot a_{H_3PO_4}^{-1}$		25	k_o 7.7	-4		
									25	k' 4.0	-3		
				$NaClO_4$		0.2	3.3	$k_1AB + k_2A^2B$	25	k_1 1.05	-3	*	(2)
						0.2	3.3		25	k_2 2.40	-3		
						0.2	4.4		25	k_1 3.2	-3		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_5B(OH)_2 + H_2O_2 \longrightarrow$	H_2O	10^2A = 1-5	$NaClO_4$		0.2	4.4	$k_1AB + k_2A^2B$	25	k_2 5.0	-2	*	(2)
	$C_6H_5OH + B(OH)_3$		10^3B = 5-40			0.2	4.5-5.5	$k'_1 = k_1[H^+]$	25	k'_1 1.2	-7		
						0.2	4.5-5.5	$k'_2 = k_2[H^+]$	25	k'_2 1.8	-6		
	(continued)					0.5	2-5	$k'_1 = k_1[H^+]$	25	k'_1 1.3	-7		(3)
						0.5	2-5	$k'_2 = k_2[H^+]$	25	k'_2 1.6	-6		
			10^2A = 2	$ClCH_2COOH$ / $ClCH_2COONa$	0.055	0.2	3.67	$k\,AB$	25	1.45	-3	*	(2)
			4			0.2	3.67		25	1.61	-3		
			2		0.22	0.2	3.75		25	1.58	-3		
			4			0.2	3.75		25	1.73	-3		
			2	CH_3COOH / CH_3COONa	0.05	0.2	4.88		25	9.92	-3		
			4			0.2	4.88		25	1.26	-2		
			1		0.05	0.2	5.24		25	1.98	-2		
			2			0.2	5.24		25	2.28	-2		
			10^3A = 4-1000;	$NaClO_4$ +				$k\,AB$				*	(3)
			$10^3B \simeq 3$	catalyst = X		0.5	~2	$k = k_o + k_xX$	25	k_o 8	-4		
				$(HOOCCH_2)_2C(OH)COOH$	0-0.2	0.5	1.9		25	k_x 1.5	0		
				$(CH_2)_5C(OH)COOH$	0-0.05	0.5	2.4		25	k_x 1.2	0		
				$(CH_3)_2C(OH)COOH$	0-0.2	0.5	2.3		25	k_x 7.5	-1		
				o-HOC_6H_4COOH	0-0.005	0.5	2.8		25	k_x 5.9	-1		
				$C_6H_5CH(OH)COOH$	0-0.05	0.5	2.2		25	k_x 3.6	-1		
				$CH_3CH(OH)COOH$	0-0.05	0.5	2.4		25	k_x 1.6	-1		
				$HOCH_2COOH$	0-0.2	0.5	2.5		25	k_x 2.5	-2		
				$HOCH_2CH_2COOH$	0-0.05	0.5	2.8		25	k_x 2	-3		
				(other chelating agents see comments)									

Supplement 1955

COMMENTS

Literature. (1) Selected data. This appears to be a unique case of acid catalysis where each strong acid gives an individual catalytic rate law. With perchloric acid as catalyst linear plot obtained on plotting log $k_{cor.}$ vs. log of the product of the activities of the water and the perchloric acid. $k_{cor.}$ is observed pseudo second order rate constant corrected for uncatalyzed reaction observed between pH = 2-3. With sulfuric acid no simple linear correlation was found between $k_{cor.}$ and the activities of the sulfuric acid and the water but log $(a^{\frac{1}{2}}_{H_2O} \times a^{3/2}_{H_2SO_4})$ vs. log $k_{cor.}$ gave a linear plot over the range studied. Only in the case of phosphoric acid was a linear relationship observed between log $k_{cor.}$ and H_o, Hammett's acidity function. (2) Selected data. In absence of buffers initial and integrated course rates obey the rate expression $-dB/dt = k_1AB + k_2A^2B$. In presence of buffer pseudo second order rate law obeyed but calculated constants dependent upon pH with slight dependence upon buffer concentration and initial concentration of A and ionic strength. (3) Selected data. Wide variety of chelating agents tested for catalytic activity. No appreciable catalytic activity observed for the simple dibasic acids used nor for any of the 1,2 or 1,3-diols studied in acetate buffer at pH = 4.7. Concentrations of malonic acid and malonate ion each at 0.5 M/l depressed rate about 35%. All α-hydroxy acids studied showed definite catalytic activity. Detailed studies made using citric acid and α-hydroxy iso-butyric acids as catalysts relating catalytic activity to pH as well as to concentrations of a variety of ions and complexes.

LITERATURE

(1) H. G. Kuivila, *ACS* 1955, **77**, 4014.

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EXCHANGE

Replacement of Boron by halogen on aromatic C

Reaction type: $ArB(OH)_2 + X_2 + H_2O \longrightarrow ArX + H_3BO_3 + HX$
(A) (B) (C) (L) (M) (N)

Rate measured: $-dB/dt$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	μ	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_5B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4	0.4	k AB	25	4.84	-3	*	(3)*
		WAc50*	$10^3A = 8-40$;				k AB	25	6.41	-3	*	(2)
			$10^3B = 2-9$	$NaClO_4$	0.12	0.12		25	7.28	-3		
				$NaNO_3$	0.3	0.3		25	7.62	-3		
				Na_2SO_4	0.1	0.3		25	1.27	-2		
				(X)			$k = k_o + k_x X$	25	$k_o = 7.28$	-3		
				$Na_2H_2PO_4$	0.06-0.12	0.12		25	$k_x = 7.2$	-2		
				CH_3COONa	0.06-0.12	0.12		25	$k_x = 3.0$	-1		
				$ClCH_2COONa$	0.06-0.12	0.12		25	$k_x = 2.5$	-1		
				$Cl_2CHCOONa$	0.06-0.12	0.12		25	$k_x = 1.33$	-1		
				C_6H_5COONa	0.06-0.12	0.12		25	$k_x = 3.27$	-1		
				$NaHSO_4$	0.3	0.3	k AB	25	5.06	-3		
				$HClO_4$	0.1	0.25		25	4.34	-3		
					0.12	0.12		25	4.16	-3		
.2	$m\text{-}CH_3C_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4	0.4	k AB	25	1.61	-2		(3)*
.3	$p\text{-}CH_3C_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4	0.4	k AB	25	3.8	-1		(3)*
.4	$p\text{-}C_6H_5C_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4	·	k AB	25	1.05	-1		(1)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	μ	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.5	p-$CH_3OC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4	0.4	k AB	25	>7	+3		([3])*
.6	p-$CH_3OC_6H_4B(OH)_2 + I_2 + H_2O \longrightarrow$	WM5*	$10^3A = 2$-10; $10^3B = 2$-16	CH_3COOH / CH_3COONa	pH = 4.42	0.74					*	([5])
					$[I^-] = 0.2$		k AB	25	2.48	-2		
					0.5			25	9.1	-3		
					0.1-0.5		$k\,[I^-]$	25	4.94	-3		
				$[CH_3COOH] = R \times [CH_3COONa]$	$[I^-] = 0.15$							
					$[CH_3COONa] =$							
				R = 9; pH = 3.6	0.0		k AB	25	6.70	-3		
				9 3.6	0.05			25	5.98	-3		
				9 3.6	0.10			25	5.27	-3		
				9 3.6	0.20			25	3.82	-3		
				9 3.6	0.40			25	1.75	-3		
				1.5 4.5	0.0			25	3.70	-2		
				1.5 4.5	0.10			25	3.50	-2		
				1.5 4.5	0.20			25	3.30	-2		
				1.5 4.5	0.40			25	2.94	-2		
				1.5 4.5	0.58			25	2.58	-2		
				0.43 5.0	0.0			25	1.20	-1		
				0.43 5.0	0.10			25	1.16	-1		
				0.43 5.0	0.20			25	1.15	-1		
				0.43 5.0	0.40			25	1.08	-1		
				0.11 5.6	0.0			25	4.39	-1		
				0.11 5.6	0.10			25	4.27	-1		
				0.11 5.6	0.20			25	4.22	-1		
				0.11 5.6	0.40			25	4.14	-1		
				pH = 4.5-5.6	0.0	0.74	$k'AB/[H^+]$	25	1.2	-6		
				3.5	0.0	0.74		25	1.76	-6		
				(Other catalysts see Supplementary Table)								

Supplement 1955

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	μ	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.7	$m\text{-}C_2H_5OOCC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4		k AB	25	2.10	-4		(3)*
.8	$p\text{-}C_2H_5OOCC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4		k AB	25	5.04	-5		(3)*
.9	$m\text{-}NO_2C_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	A = 0.08	NaBr	0.4		k AB	25	1.46	-5		(3)*
.10	$m\text{-}FC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4		k AB	25	1.87	-4		(1)
.11	$p\text{-}FC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	$10^2A = 1$; $10^3B = 8$	NaBr	0.4		k AB	25	1.36	-2		(1)
.12	$m\text{-}ClC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	C	$10^3A = 2\text{-}10$; $10^3B = 2.5\text{-}20$	$[CH_3COOH] = R[CH_3COONa]$	$[Br^-] = 0.25$ $[CH_3COOH] =$	0.70					*	(4)
			R = 0.67	pH = 4.7	0		k AB	25	3.55	-1		
			0.67	4.7	0.15			25	3.60	-1		
			0.67	4.7	0.30			25	3.39	-1		
			0.67	4.7	0.45			25	3.20	-1		
			1.22	4.4	0			25	1.77	-1		
			1.22	4.4	0.15			25	1.60	-1		
			1.22	4.4	0.30			25	1.59	-1		
			1.22	4.4	0.45			25	1.50	-1		
			2.33	4.1	0			25	9.55	-2		
			2.33	4.1	0.12			25	8.76	-2		
			2.33	4.1	0.30			25	7.67	-2		
			2.33	4.1	0.45			25	6.66	-2		
			5.7	3.7	0			25	3.70	-2		
			5.7	3.7	0.15			25	2.75	-2		
			5.7	3.7	0.30			25	2.20	-2		
			5.7	3.7	0.45			25	1.47	-2		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	μ	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.12	m-$ClC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$ *(continued)*	C	10^3A = 2-10; 10^3B = 2.5-20	$CH_2ClCOOH$ $CH_2ClCOONa$ (Other catalysts see Supplementary Table)	$[Br^-]$ = 0.25 pH = 2-3	0.70	k AB/ $[H^+]$	25	7	-6	*	(4)
.13	p-$ClC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	10^2A = 1; 10^3B = 8	NaBr	0.4		k AB	25	2.61	-3		(3)*
.14	m-$BrC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	10^2A = 1; 10^3B = 8	NaBr	0.4		k AB	25	2.13	-4		(1)
.15	p-$BrC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	10^2A = 1; 10^3B = 8	NaBr	0.4		k AB	25	2.00	-3		(3)*
.16	m-$IC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	10^2A = 1; 10^3B = 8	NaBr	0.4		k AB	25	3.46	-4		(1)
.17	p-$IC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$	WAc20*	10^2A = 1; 10^3B = 8	NaBr	0.4		k AB	25	2.41	-3		(1)

SUPPLEMENTARY TABLE

(.6) p-$CH_3OC_6H_4B(OH)_2 + I_2 + H_2O \longrightarrow$ (5)

Solvent H_2O + 5 vol % CH_3OH 10^3A = 2-10 10^3B = 2-16

μ = 0.70; pH = 4.48; NaI = 0.15; CH_3COOH = 0.45; CH_3COONa = 0.30

$k = 3.20 \times 10^{-2} + k_1[\text{catalyst}]$

(continued on next page)

SUPPLEMENTARY TABLE *(continued)*

	Catalyst	$10^3 \times$ max. [catalyst]	k'
(.6) *continued*	H_3BO_3	100	0.048
	$(CH_3)_2C(NH_2)CH_2OH$	9.4	0.172
	cis-indane-1,2-diol	1.0	7.0
	cis-indane-1,2-diol }	1.0	10.4
	H_3BO_3 }	100	
	$HOCH_2COOH$	2.0	16.1
	NaF	2.0	39.4
	5-NO_2-salicylic acid	2.0	39.3
	tartaric acid	2.0	80.0
	salicylic acid	2.0	184

No catalytic effect with ethylene glycol, pinacol, 2,3-butanediol, or *cis*-cyclohexane-1,2-diol.

(.12) $m\text{-}ClC_6H_4B(OH)_2 + Br_2 + H_2O \longrightarrow$ [4]

solvent: H_2O; $10^3A = 2\text{-}10$; $10^3B = 2.5\text{-}20$

$\mu = 0.70$; pH = 2.62; NaBr = 0.25; $CH_2ClCOOH = 0.45$; $CH_2ClCOONa = 0.45$

$k = 3.79 \times 10^{-3} + k'[\text{catalyst}]$

Catalyst	10^3 [catalyst]	k'
$HOCH_2COOH$	1-4	1.8
citric acid	2-4	2.75
$(CH_3)_2C(OH)COOH$	1-2	16.4
d-tartaric acid	1-2	16.4
NaF	1-2	21.8
cis-cyclohexane-1,2-diol	1-3	<0.1

SOLVENTS

WAc20*(50)	H_2O + indicated vol % CH_3COOH
WM5*	H_2O + 5 vol % CH_3OH

COMMENTS

Literature: ([3]) Authors stated that rate of replacement of boronic acid and anhydride were identical and did not designate which form was used in rate experiments.

Reactions: **(.1)** Inhibition by acids but specific base catalysis observed. **(.6)** Reactive species considered to be I_2 and boronate anion from dependence of rate upon $[I^-]^{-1}$ and $[H^+]^{-1}$. In presence of acetate buffer rate constant may be expressed by equation $k = k_o\{1-0.216[CH_3COOH]-0.145[CH_3COONa]\}$ where k_o is a function of pH or buffer ratio and is the tabulated value extrapolated to zero concentration of buffer. For specific catalyst effects see Supplementary Table. **(.12)** Reactive species considered to be Br_2 and boronate anion as plot of rate constant versus fraction of free Br_2 gives linear plot through origin and rate also proportional to $[H^+]^{-1}$. Tetra covalent boron in anion probable from specific catalytic activity of F^- and chelating agents. For special catalytic effects see Supplementary Table. In acetate buffer rate constant may be expressed by equation $k = k_o\{1-0.233[CH_3COOH]-0.070[CH_3COONa]\}$ where k_o is a function of pH or buffer ratio and is the tabulated value extrapolated to zero buffer concentration.

LITERATURE

([1]) H.G. Kuivila, L.E. Benjamin, *ACS* 1955, **77**, 4834.

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([3]) H.G. Kuivila, A.R. Hendrickson, *ACS* 1952, **74**, 5068.

([4]) H.G. Kuivila, E.J. Soboczenski, *ACS* 1954, **76**, 2675.

([5]) H.G. Kuivila, R.M. Williams, *ACS* 1954, **76**, 2679.

EXCHANGE

Replacement of C by N on aromatic C

Reaction type: $ArCOOH + HN_3 \longrightarrow ArNH_2 + N_2 + CO_2$
(A) (B) (L) (M) (N)

Liquid phase

Amounts are in M/l. Rates and rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_5COOH + HN_3 \longrightarrow C_6H_5NH_2 + N_2 + CO_2$	H_2SO_4 95.4 %	A = B = 0.05			k AB	25		1.98	-4	*	(1)
		$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	180			*	(2)
.2	$m\text{-}CH_3C_6H_4COOH + HN_3 \longrightarrow m\text{-}CH_3C_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	120			*	(2)
.3	$p\text{-}CH_3C_6H_4COOH + HN_3 \longrightarrow p\text{-}CH_3C_6H_4NH_2 + N_2 + CO_2$	H_2SO_4 95.4 %	A = B = 0.05			k AB	25		3.71	-4	*	(1)
.4	$m\text{-}HOC_6H_4COOH + HN_3 \longrightarrow m\text{-}HOC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	300			*	(2)
.5	$o\text{-}CH_3OC_6H_4COOH + HN_3 \longrightarrow o\text{-}CH_3OC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	300			*	(2)
.6	$m\text{-}CH_3OC_6H_4COOH + HN_3 \longrightarrow m\text{-}CH_3OC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	240			*	(2)
.7	$p\text{-}CH_3OC_6H_4COOH + HN_3 \longrightarrow p\text{-}CH_3OC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	90			*	(2)
.8	$m\text{-}C_2H_5OC_6H_4COOH + HN_3 \longrightarrow m\text{-}C_2H_5OC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	240			*	(2)
.9	$m\text{-}HOOCC_6H_4COOH + HN_3 \longrightarrow m\text{-}HOOCC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	1,020			*	(2)
.10	$m\text{-}N{:}CC_6H_4COOH + HN_3 \longrightarrow m\text{-}N{:}CC_6H_4NH_2, N_2, CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	1,080			*	(2)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.11	$o\text{-}NO_2C_6H_4COOH + HN_3 \longrightarrow o\text{-}NO_2C_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	120			*	(2)
.12	$m\text{-}NO_2C_6H_4COOH + HN_3 \longrightarrow m\text{-}NO_2C_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	6,000			*	(2)
.13	$p\text{-}NO_2C_6H_4COOH + HN_3 \longrightarrow p\text{-}NO_2C_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	7,200			*	(2)
.14	$m\text{-}ClC_6H_4COOH + HN_3 \longrightarrow m\text{-}ClC_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	720			*	(2)
.15	$m\text{-}BrC_6H_4COOH + HN_3 \longrightarrow m\text{-}BrC_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	600			*	(2)
.16	$m\text{-}IC_6H_4COOH + HN_3 \longrightarrow m\text{-}IC_6H_4NH_2,\ N_2,\ CO_2$	$ClHC{:}CCl_2$	A= 2.5; B= 0.25	H_2SO_4	1.5		40	900			*	(2)
.17	$C_{14}H_8O_2 + 2HN_3 + H_2O \longrightarrow C_{13}H_9ON + 2N_2 + CO_2 + NH_3$ (phenanthrenequinone) (phenanthridone)	H_2SO_4 98.5 %	A ≃ 0.02; B = 0.05-0.1		-dA/dt = k AB		25		4.1	-2	*	(1)
		96.8					25		1.14	-1		
		95.4					25		1.57	-1		
		92.5					25		3.82	-1		
		84.3					25		2.32	0		
			-dB/dt = k AB + k'IB; dL/dt = dN/dt = k'IB; (I = intermediate)									
		98.5					25		3.58	-3		
		96.8					25		2.1	-3		
		95.4					25		1.6	-3		
		92.5					25		1.02	-3		
		84.3					25		0.76	-3		

COMMENTS

Literature. ([2]) Units, seconds converted from original minutes.

Reaction. **(.1)** No appreciable decomposition of B during reaction time but ([1]) observed unreliable results with substituted benzoic acid due to decomposition in H_2SO_4 solvent. Aniline sulfate is final product. ([2]) observed ratio of L/M = 0.70. **(.2)** L/M = 0.53. **(.3)** No appreciable decomposition of B during reaction time. **(.4)** L/M = 0.88. **(.5)** L/M = 0.81. **(.6)** L/M = 0.87. **(.7)** L/M = 0.86. **(.8)** L/M = 0.83. **(.9)** L/M = 0.71. **(.10)** L/M = 0.82. **(.11)** L/M = 0.71. **(.12)** L/M = 0.82. **(.13)** L/M = 0.59. **(.14) (.15) (.16)** L/M = 0.78. **(.17)** Reaction involves consecutive reactions. The first reaction forms an intermediate which reacts with a second molecule of B to form final products. Rate expression broken up into initial k AB and following k'IB rate laws. Where I represents concentration of intermediate.

LITERATURE

([1]) T. Bak, *Acta. Chem. Scand.* 1954, **8**, 1733. ([2]) L.H. Briggs, J.W. Lyttleton, *CSL* **1943**, 421.

EXCHANGE

Replacement of C by sulfate on Si

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$HOOCCH_2CH_2Si(CH_3)_3 + H_2SO_4 \longrightarrow HOOCCH_2CH_2Si(CH_3)_2SO_4H + CH_4$	85-97% $H_2SO_4 + H_2O$	A= 0.05; B= 3-22	$NaHSO_4$	not stated	k AB	20	1.4	-4

COMMENTS

Reaction pseudo first order with respect to A. Second order constant calculated by dividing pseudo first order constant by calculated concentration of molecular H_2SO_4. This was varied from 2.9 to 22 by adjusting the H_2O concentration. Addition of $NaHSO_4$ gave a very small salt effect.

LITERATURE

L.H. Sommer, W.P. Barie, J. Gould, *ACS* 1953, 75, 3765.

EXCHANGE

Replacement of C by halogen on Aromatic C

Reaction type: $ArCOOH + X_2 \longrightarrow ArX + CO_2 + HX$

(A) (B) (L) (M) (N)

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1)	Amount of addend (1)	Addend (2)	Amount of addend (2)	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$2\text{-OH-3,5-Br}_2C_6H_2COOH + Br_2 \longrightarrow 1,3,5\text{-Br}_3\text{-2-HOC}_6H_2 + CO_2 + HBr$	AcW 75*	$10^3A = 5$; $10^3B = 4$-8	$HClO_4$	0.10			k AB	20	5.8	-2
			" 8		0.30				20	2.55	-2
			" 5		0.10	$KClO_4$	0.004		20	5.6	-2
			" 7		0.10	KBr	0.004		20	4.7	-2
			" 8		0.29	HBr	0.01		20	1.35	-2
			" 8		0.25		0.05		20	3.47	-3
			" 8		0.20		0.1		20	1.37	-3
			" 8		0.10		0.2		20	4.40	-4
			" 8		0		0.3		20	2.33	-4
			" 4		0.10	LiBr	0.10		20	4.9	-3
			" 8	HBr	0.30		0		20	2.33	-4
			" 8		0.20		0.10		20	4.28	-4
			" 8		0.10		0.20		20	1.15	-3
		AcW 70*	" 8		0.30		0		20	1.18	-3
		AcW 80*	" 8		0.30		0		20	2.93	-5
.2	$4\text{-OH-3,5-Br}_2C_6H_2COOH + Br_2 \longrightarrow 1,3,5\text{-Br}_3\text{-4-HOC}_6H_2 + CO_2 + HBr$	AcW 80*	$10^3A = 5$; $10^3B = 6$	$HClO_4$	0.10			k AB	20	6.3	-1
			" 4-8		0.10	LiBr	0.10		20	1.30	-2
			" 8		0.05		0.10		20	3.4	-2
			" 8		0.300				20	3.00	-1
			" 8		0.250	HBr	0.050		20	7.6	-3
			" 8		0.200		0.100		20	1.82	-3

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1)	Amount of addend (1)	Addend (2)	Amount of addend (2)	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n
.2	$4\text{-OH-3,5-Br}_2\text{C}_6\text{H}_2\text{COOH} + \text{Br}_2 \longrightarrow 1,3,5\text{-Br}_3\text{-4-HOC}_6\text{H}_2 + \text{CO}_2 + \text{HBr}$ *(continued)*	AcW 75*	10^3A= 5; 10^3B= 8	$HClO_4$		HBr	0.300	k AB	20	1.97	-3
		AcW 70*	" 8				0.300		20	1.16	-2

COMMENTS

(.1) Selected data. Rate constant fits the equation

$$k[Br_2][H^+]/(Br_2) = \frac{(0.0103[H^+] + 0.0042)}{49(H^+)^2(Br^-) + 20[H^+][Br^-] + 1}$$

where $[Br_2]$ represents total Br_2 concentration and (Br_2) represents actual concentration of free Br_2.

(.2) Selected data. Rate constant will fit an equation similar to that for reaction (.1) but it also fits the equation

$$\frac{k K_1 [Br_2][Br^-]}{[Br_3^-]} = 2.5 + 0.60[H^+]^{-1}$$

where $[Br_2]$ represents the total concentration of Br_2 in all forms.

LITERATURE

E. Grovenstein, U.V. Henderson, *ACS* 1956, **78**, 569.

EXCHANGE

Replacement of Si by halogen on aromatic C

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
.1	$C_6H_5Si(CH_3)_3 + Br_2 \longrightarrow C_6H_5Br + (CH_3)_3SiBr$	CCl_4	A = 0.06-0.4; B = 0.04-0.14	$k\,AB^2$	35	1.68	-3	
					40	2.12	-3	
		$C_6H_5NO_2$		(too rapid to measure)				
.2	$o\text{-}NO_2C_6H_4Si(CH_3)_3 + Br_2 \longrightarrow o\text{-}NO_2C_6H_4Br + (CH_3)_3SiBr$	$C_6H_5NO_2$		$k\,AB^2$	40	2	-4	*
.3	$m\text{-}NO_2C_6H_4Si(CH_3)_3 + Br_2 \longrightarrow m\text{-}NO_2C_6H_4Br + (CH_3)_3SiBr$	$C_6H_5NO_2$		$k\,AB^2$	40	2.5	-3	*
.4	$p\text{-}NO_2C_6H_4Si(CH_3)_3 + Br_2 \longrightarrow p\text{-}NO_2C_6H_4Br + (CH_3)_3SiBr$	$C_6H_5NO_2$		$k\,AB^2$	40	1	-3	*
.5	$\underbrace{SCBr{:}CHCH{:}C}Si(CH_3)_3 + Br_2 \longrightarrow \underbrace{SCBr{:}CHCH{:}C}Br + (CH_3)_3SiBr$ (2-bromo-5-trimethylsilylthiophene)	CCl_4		$k\,AB^2$	35	4.5	-2	

COMMENTS

Reactions. (.2) (.3) (.4) Order of reaction not definitely established in $C_6H_5NO_2$ as complicated by side reactions and slowness of reaction. Rate constant gives only order of magnitude.

LITERATURE

R. A. Benkeser, A. Torkelson, *ACS* 1954, **76**, 1252.

EXCHANGE

Replacement of N by O on aliphatic C

Reaction types: $RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$

$RNH_3^+ + HNO_2 \longrightarrow ROH + N_2 + H_3O^+$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$CH_3NH_3^+ + HNO_2 \longrightarrow$ $CH_3OH + N_2 + H_3O^+$	H_2O	A= 0.2-1; B= 0.004-0.2	$H_2PO_4^-$, $HPO_4^=$	0.50	1.1	k AB	20	1.91	-4				*	(2)
						1.1		25	2.91	-4					
						1.12		30	4.23	-4					
						2.10		30	4.02	-4					
						2.70		30	3.21	-4					
						3.70		30	1.03	-4					
						4.50		30	1.87	-5					
						1.1		35	6.4	-4	14	3	9		
			A= 0.05-0.1; B= 0.05-0.1	NO_2^-	0.05		k AB[NO_2^-]	25	1.8	-2					(3)
.2	$CH_3CH_2CH_2NH_3^+ + HNO_2 \longrightarrow$ $CH_3CH_2CH_2OH$, $(CH_3)_2CHOH + N_2 + H_3O^+$	H_2O	A= 0.05-0.1; B= 0.05-0.1	NO_2^-	0.05		k AB[NO_2^-]	25	1.1	-2				*	(5)
.3	$HOOCCH_2NH_2 + HNO_2 \longrightarrow$ $HOOCCH_2OH + N_2 + H_2O$	H_2O	10^3A= 3-50; 10^2B= 2-5	H_2SO_4	0.05-0.1		k AB^2	25	4.0	-1				*	(1) (4)
.4	$HOOCCH_2CH_2NH_2 + HNO_2 \longrightarrow$ $HOOCCH_2CH_2OH + N_2 + H_2O$	H_2O	10^2A= 2-5; 10^2B= 2-5	H_2SO_4	0.05-0.1		k AB^2	25	5.8	-2				*	(4)
.5	$HOOC(CH_3)CHNH_2 + HNO_2 \longrightarrow$ $HOOC(CH_3)CHOH + N_2 + H_2O$	H_2O	10^2A= 2-5; 10^2B= 2-5	H_2SO_4	0.05-0.1		k AB^2	25	2.0	-1				*	(4)

COMMENTS

Reaction. **(.1)** Initial rate measured by ([2]) and rate constant calculated by dividing initial rate by total concentrations of A and B. Increase in ionic strength from 0.50 to 1.50 depresses rate constant from 5.0×10^{-4} to 3.5×10^{-4}. Change in buffer concentration from 0.25 to 0.75 had no effect on rate. Pseudo second order rate constant over reaction course observed by ([3]). Third order constant calculated by dividing by concentration of nitrite ion. Units, seconds converted from original minutes. **(.2)** Third order rate law followed up to 20% reaction. Units, seconds converted from original minutes. **(.3)** Reaction found to follow three different rate laws by ([1]): $k' = 2.0 \times 10^{-4}$ for $k'[HOOCCH_2NH_3^+]B^2$; $k_3 = 4.3$ for $k_3[HOOCCH_2NH_3^+]B[NO_2^-]$ and $k\,AB^2$. Each appeared to have some advantage at appropriate conditions, but no one expression was valid over entire range studied by ([1]). Units, seconds converted from original minutes. Negative salt effect observed by ([4]) also rate depressed by H_2SO_4. Rate constant extrapolated to zero time as they decreased with course of reaction. **(.4) (.5)** Rate constants extrapolated to zero time as they decreased with course of reaction. Units seconds converted from original minutes.

LITERATURE

([1]) E. Abel, H. Schmid, W. Sidon, *ZEC* 1933, **39**, 863. ([2]) J.H. Dusenbury, R.E. Powell, *ACS* 1951, **73**, 3269. ([3]) T.W.J. Taylor, *CSL* **1928**, 1099. ([4]) T.W.J. Taylor, *CSL* **1928**, 1897. ([5]) T.W.J. Taylor, L.S. Price, *CSL* **1929**, 2052.

EXCHANGE

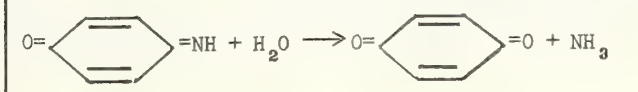
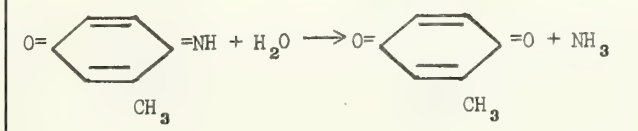
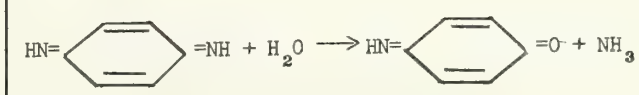
Replacement of N= by O= on aromatic C

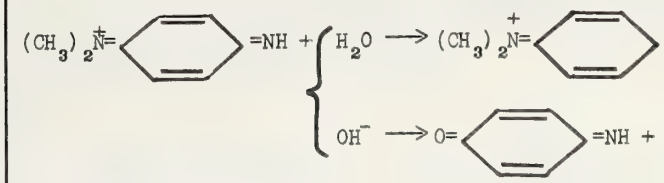
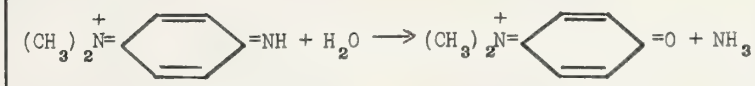
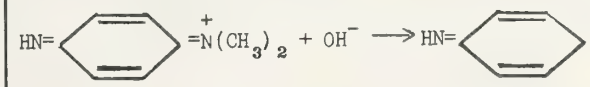
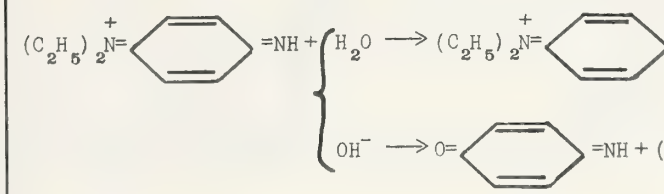
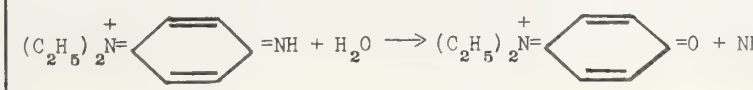
Liquid phase

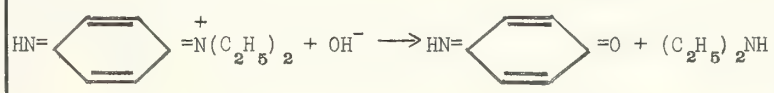
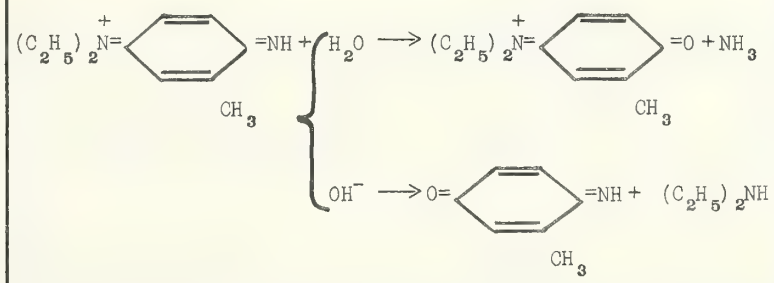
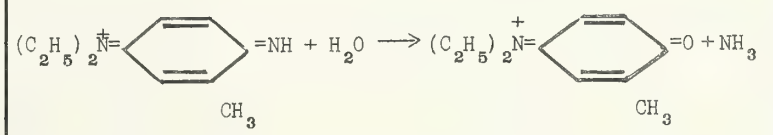
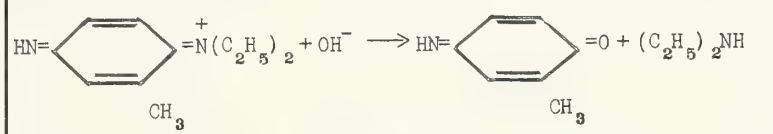
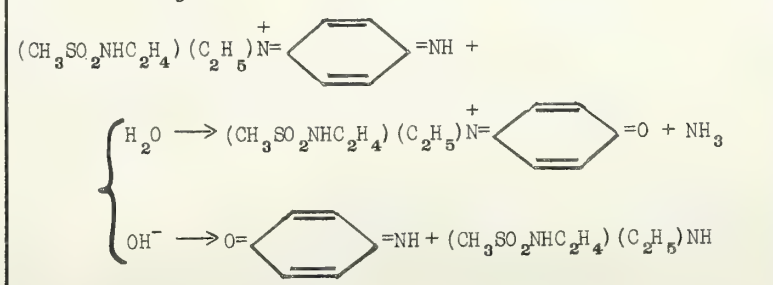
Amounts are in M/l. Rate constants are in M/l and sec.

Reaction types: $Ar{:}NR_1R_1^+ + OH^- \longrightarrow Ar{:}O + R_1R_2NH$

$Ar{:}NR + H_2O \longrightarrow Ar{:}O + RNH_2$

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1		H_2O	$10^4A = 2.5$	$H_2PO_4^-$, $HPO_4^=$, $Fe(CN)_6^{-3}$	6.1	kA	25	1.54	-3	*	(1)
					7.1		25	5.5	-4		
					8.0		25	1.92	-4		
					8.7		25	1.31	-4		
					9.8		25	1.15	-4		
					11.0		25	1.54	-4		
					11.9		25	3.84	-4		
.2		H_2O	$10^4A = 2.5$	$H_2PO_4^-$, $HPO_4^=$, $Fe(CN)_6^{-3}$	6.1	kA	25	1.62	-3	*	(1)
					7.1		25	7.1	-4		
					8.0		25	1.6	-4		
					8.8		25	1.2	-4		
					10.0		25	8	-5		
					12.0		25	1.8	-4		
.3		H_2O	$10^4A = 1.25$	$H_2PO_4^-$, $HPO_4^=$, $Fe(CN)_6^{-3}$	6.1	kA	25	6.34	-3	*	(1)
					7.0		25	1.04	-4		
					8.0		25	4.3	-4		
					8.9		25	3.5	-4		
					10.2-12.2		25	3.3	-4		
			$\mu = 0.008-0.06$	OH^-	11.4		25	2.9	-4		(2)

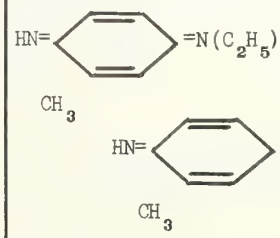
No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.4		H_2O	$10^4A = 1.88$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	7.1	$kA = -dA/dt$	25	2.5	-3	*	(1)
					8.0	$k = k' + k''[OH^-]$	25	1.63	-2		
					10.0		25	2.53	0		
					11.1		25	3.04	+1		
					12.0		25	1.96	+2		
.4.1		H_2O	(calculated using .4 and .1)		7.1	$k'A = dL/dt$	25	5	-4	*	(1)
					8.0		25	1.8	-3		
.4.2		H_2O	(calculated using .4 and .1)		7-12	$k''AB = dL/dt$	25	2.5	+4	*	(1)
.5		H_2O	$10^4A = 1.2-1.9$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	6.1	$kA = -dA/dt$	25	5.46	-4	*	(1)
					7.1	$k = k' + k''[OH^-]$	25	1.10	-3		
					8.0		25	6.48	-3		
					9.0		25	5.72	-2		
					10.1		25	1.24	0		
					11.1		25	1.11	+1		
					12.0		25	7.76	+1		
.5.1		H_2O	(calculated using .5 and .1)		7.1	$k'A = dL/dt$	25	3	-4	*	(1)
					8.0		25	2	-4		
					9.0		25	~10	-3		

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.5.2		H_2O	(calculated using .5 and .1)		7-9	$k''AB = dL/dt$	25	6.2	+3	*	(1)
					10.1		25	9	+3		
					11-12		25	8.6	+3		
.6		H_2O	$10^4A = 1.2-7.5$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	7.0	$kA = -dA/dt$	25	3.90	-4	* (1) (2)	
					8.0	$k = k' + k''[OH^-]$	25	1.12	-3		
					8.9		25	8.65	-3		
					10.0		25	1.41	-1		
					11.1		25	2.00	0		
					11.9		25	1.32	+1		
.6.1		H_2O	(calculated using .6 and .2)		7-8	$k'A = dL/dt$	25	2.9	-4	*	(1)
.6.2		H_2O	(calculated from .6 and .2)		7-12	$k''AB = dL/dt$	25	1.66	+3	*	(1)
.7		H_2O	$10^4A = 1.9$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	8.0	$kA = -dA/dt$	25	8.1	-2	*	(1)
					8.6		25	1.22	-1		
					10.1		25	1.77	-1		
					11.1		25	4.21	-1		
					12.0		25	2.16	0		
							25	k' 2	+4		
							25	k'' 2.2	+2		
							25	K 1.3	-9		

$$k = [OH^-]\left\{k'\left(1 - \frac{K[OH^-]}{K[OH^-] + 10^{-14}}\right) + \frac{k''K[OH^-]}{K[OH^-] + 10^{-14}}\right\}$$

Supplement 1956

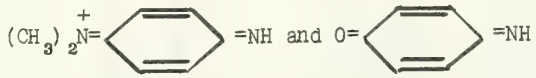
No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.8	$(CH_3SO_2NHC_2H_4)(C_2H_5)\overset{+}{N}=$ $=NH +$	H_2O	$10^4A = 1.9$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	8.0	$kA = -dA/dt$	25	2.14	-2	*	(1)
					8.6		25	3.19	-2		
					10.1		25	1.66	-1		
					11.0		25	5.19	-1		
					11.9		25	2.86	0		
	$H_2O \longrightarrow (CH_3SO_2NHC_2H_4)(C_2H_5)\overset{+}{N}=$ $=O + NH_3$						25	k' 4.5	+3		
	$OH^- \longrightarrow O=$ $=NH + (CH_3SO_2NHC_2H_4)(C_2H_5)NH$		$k = [OH^-]\{k'(1 - \frac{K[OH^-]}{K[OH^-] + 10^{-14}}) + \frac{k''K[OH^-]}{K[OH^-] + 10^{-14}}\}$				25	k'' 3	+2		
							25	K 3	-10		
.9	$[CH_3SO_2N(CH_3)C_2H_4](C_2H_5)\overset{+}{N}=$ $=NH +$	H_2O	$10^4A = 1.25$	$H_2PO_4^-$, $HPO_4^{=}$, $Fe(CN)_6^{-3}$	7.0	$kA = -dA/dt$	25	8.7	-4	*	(1)
					8.1		25	5.5	-3		(1) (2)
					8.9	$k = k' + k''[OH^-]$	25	3.3	-2		
					10.1		25	8.5	-1		
					11.1		25	7.3	0		
					12.0		25	5.5	+1		
	$H_2O \longrightarrow [CH_3SO_2N(CH_3)C_2H_4](C_2H_5)\overset{+}{N}=$ $=O + NH_3$										
	$OH^- \longrightarrow O=$ $=NH + [CH_3SO_2N(CH_3)C_2H_4](C_2H_5)NH$										
.9.1	$[CH_3SO_2N(CH_3)C_2H_4](C_2H_5)\overset{+}{N}=$ $=NH + H_2O \longrightarrow$	H_2O	(calculated using .9 and .2)		8	$k'A = dL/dt$	25	~5	-4	*	(1)
	$[CH_3SO_2N(CH_3)C_2H_4](C_2H_5)\overset{+}{N}=$ $=O + NH_3$										

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.9.2		H_2O	(calculated using .9 and .2)		7-12	$k''AB = dL/dt$	25	6.0	+3	*	([1])

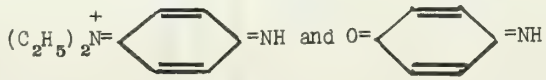
COMMENTS

General. All reactions carried out at constant pH in presence of buffer, and in presence of excess $K_3Fe(CN)_6$ used to form A by oxidation of corresponding *p*-phenol amine or *p*-phenyl diamine. At high pH the quinones produced may react further with the $K_3Fe(CN)_6$. Reactions followed spectrophotometrically for dyes produced by a coupling reaction with α-napthol.

Reaction. **(.4)** Consists of parallel reactions (.4.1) and (.4.2) with consecutive reaction (.1) following (.4.2). **(.4.1) (.4.2)** Parallel reactions kinetically separated by following concentrations of the two dyes produced by coupling reactions of:

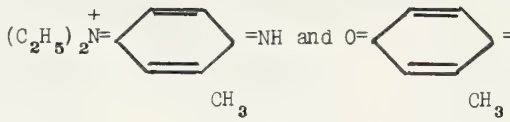


with α-napthol. This combined with measured rate of (.1) allowed calculation of rate constant for (.4.2). Values for (.4.1) were obtained by difference and give only order of magnitude. **(.5)** Consists of parallel reactions (.5.1) and (.5.2) with consecutive reaction (.1) following (.5.2). **(.5.1) (.5.2)** Parallel reactions kinetically separated by following the concentrations of the two dyes produced by coupling reactions of:

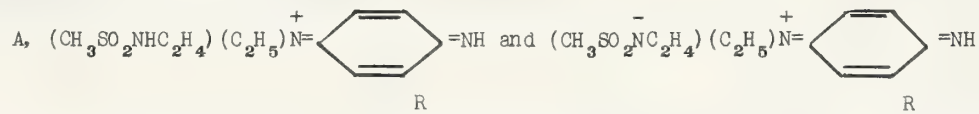


COMMENTS *(continued)*

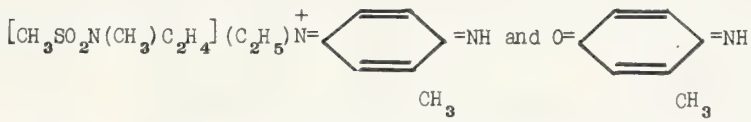
with α-napthol. This combined with measured rate of (.1) allowed calculation of rate constant for (.5.2). Values for (.5.1) were obtained by difference and give only order of magnitude. **(.6)** Consists of parallel reactions (.6.1) and (.6.2) with consecutive reactions (.2) following (.6.2). Plot of log k/k_0 vs. μ has slope = −1, see ([2]). **(.6.1) (.6.2)** Parallel reactions kinetically separated by following the concentrations of the two dyes produced by coupling reactions of



This combined with measured rate of (.2) allowed calculations of rate constant for (.6.2). Values for (.6.1) were obtained by difference and give only order of magnitude. **(.7) (.8)** Non-linear dependence of log k with pH accounted for in terms of rapid equilibrium between acid and basic forms of :



with separate rate constants k' and k'' respectively and equilibrium constant K. **(.9)** Consists of parallel reactions (.9.1) and (.9.2) with consecutive reaction (.2) following (.9.2). Shown by ([2]) to be independent of ionic strength **(.9.1) (.9.2)** Parallel reactions kinetically separated by following concentrations of the two dyes produced by coupling reactions of :



with α-napthol. This combined with measured rate of (.2) allowed calculation of rate constant for (.9.2). Values for (.9.1) were obtained by difference and give only order of magnitude.

LITERATURE

([1]) L.K.J. Tong, *J.P.C.* 1954, **58**, 1090. ([2]) L.K.J. Tong, M.C. Glesman, *ACS* 1956, **78**, 5827.

EXCHANGE

Replacement of $ArSO_3$, $(ArSO_2)$, $(ArSO)$ by $NR'R''R'''$

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments
.1	$2,4\text{-}(NO_2)_2C_6H_3SOC_6H_5 + 2\,\overline{CH_2(CH_2)_4NH} \longrightarrow$	CH_3OH	$A \simeq 0.04$; $10^3B \simeq 1$			k AB	0	2.05	-3				*
	$2,4\text{-}(NO_2)_2C_6H_3\overline{N(CH_2)_4CH_2} + \overline{CH_2(CH_2)_4NH_2}^+, C_6H_5SO^-$						25	1.09	-2				
							46	3.20	-2				
				$C_5H_{10}NH_2^+Cl^-$	0.02		0	2.15	-3				
					0.02		25	1.20	-2				
					0.02		46	3.94	-2	10.8	1.0	6	
.2	$2,4\text{-}(NO_2)_2C_6H_3SO_2C_6H_5 + 2\,\overline{CH_2(CH_2)_4NH} \longrightarrow$	CH_3OH	$A \simeq 0.04$; $10^3B \simeq 1$			k AB	0	1.43	-3				*
	$2,4\text{-}(NO_2)_2C_6H_3\overline{N(CH_2)_4CH_2} + \overline{CH_2(CH_2)_4NH_2}^+, C_6H_5SO_2^-$						25	9.30	-3				
				$C_5H_{10}NH_2^+Cl^-$	0.02		0	1.50	-3				
					0.02		25	9.56	-3	12.0	6	6	
.3	$2,4\text{-}(NO_2)_2C_6H_3OSO_2C_6H_4\text{-}p\text{-}CH_3 + 2\,\overline{CH_2(CH_2)_4NH} \longrightarrow$	CH_3OH	$A \simeq 0.04$; $10^3B \simeq 1$			k AB	0	4.54	-2				*
	$2,4\text{-}(NO_2)_2C_6H_3\overline{N(CH_2)_4CH_2} + \overline{CH_2(CH_2)_4NH_2}^+, p\text{-}CH_3C_6H_4OSO_2^-$			$C_5H_{10}NH_2^+Cl^-$	0.02		0	4.42	-2				

COMMENTS

Pseudo first order rate constants observed as A in excess. Second order constant calculated by dividing pseudo first order constant by initial concentration of A and multiplying by ratio of observed to theoretical yield of L. Competing side reactions involving solvent probably responsible for low yields of L. (.1) In absence of $\overline{CH_2(CH_2)_4}NH_2^+Cl^-$ yield only 25% which increased to 73% in presence of piperidine salt. (.2) Yield of L 92% in absence of $\overline{CH_2(CH_2)_4}NH_2^+Cl^-$ and 100% in presence of the piperidine salt. (.3) Yield of L 55% in absence of piperidine salt and 58% in its presence.

LITERATURE

J. F. Bunnett, E. W. Garbisch, K. M. Pruitt, *ACS* 1957, **79**, 385.

EXCHANGE

Replacement of Halogen by C of enolate

Reaction type: $RX + (ArC{:}OCR'R'')^{-}Na^{+} \longrightarrow ArC{:}OCRR'R'' + NaX$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

General comments at end of Table.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n
.1	$CH_3I + [C_6H_5C{:}OC(CH_3)_2]^{-}Na^{+} \longrightarrow C_6H_5C{:}OC(CH_3)_3 + NaI$	$(C_2H_5)_2O$	A= 1.7; B= 0.11	k AB	30	4.6	-4
.2	$C_2H_5Br + [C_6H_5C{:}OCH_2]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH_2C_2H_5 + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.095	k AB	30	1.0	-6
.3	$C_2H_5Br + [C_6H_5C{:}OCHCH_3]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(CH_3)C_2H_5 + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.14	k AB	30	1.6	-6
.4	$C_2H_5Br + [C_6H_5C{:}OCHC_2H_5]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(C_2H_5)_2 + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.094	k AB	30	1.0	-6
.5	$C_2H_5Br + [C_6H_5C{:}OC(CH_3)_2]^{-}Na^{+} \longrightarrow C_6H_5C{:}OC(CH_3)_2C_2H_5 + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.13	k AB	30	1.0	-6
.6	$C_2H_5Br + [C_6H_5C{:}OCHCH_2CH_2CH_3]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(C_2H_5)(C_3H_7) + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.14	k AB	30	9	-7
.7	$C_2H_5Br + [C_6H_5C{:}OCH(n\text{-}C_4H_9)]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(C_2H_5)(n\text{-}C_4H_9) + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.14	k AB	30	8	-7
.8	$C_2H_5Br + [C_6H_5C{:}OCH(n\text{-}C_7H_{13})]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(C_2H_5)(n\text{-}C_7H_{13}) + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.14	k AB	30	8	-7
.9	$C_2H_5I + [C_6H_5C{:}OCH(C_2H_5)]^{-}Na^{+} \longrightarrow C_6H_5C{:}OCH(C_2H_5)_2 + NaI$	$(C_2H_5)_2O$	A= 1.7; B= 0.096	k AB	30	1.3	-5
.10	$C_2H_5I + [C_6H_5C{:}OC(C_2H_5)_2]^{-}Na^{+} \longrightarrow C_6H_5C{:}OC(C_2H_5)_3 + NaI$	$(C_2H_5)_2O$	A= 1.7; B= 0.07	k AB	30	3.7	-6

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n
.11	$CH_3CH_2CHBr + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)(C_3H_7) + NaBr$	$(C_2H_5)_2O$	A= 1.7; B=0.09	k AB	30	3.4	-7
.12	$(CH_3)_2CHBr + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)[CH(CH_3)_2] + NaBr$	$(C_2H_5)_2O$	A= 1.7; B=0.09	k AB	30	1.5	-8
.13	$(CH_3)_2CHCH_2Br + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)[CH_2CH(CH_3)_2] + NaBr$	$(C_2H_5)_2O$	A= 1.7; B=0.09	k AB	30	4.3	-8
.14	$(CH_3)_3CBr + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)[C(CH_3)_3] + NaBr$	$(C_2H_5)_2O$	A= 1.7; B= 0.086	k AB	30	7.2	-8
.15	$(CH_3)_3CCH_2Br + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)[CH_2C(CH_3)_3] + NaBr$	$(C_2H_5)_2O$	A= 1.7; B=0.087	k AB	30	< 1	-10
.16	$C_6H_5CH_2Cl + [C_6H_5C{:}OCHCH_3]^-Na^+ \longrightarrow C_6H_5C{:}OCH(CH_3)CH_2C_6H_5 + NaCl$	$(C_2H_5)_2O$	A= 1.7; B=0.13	k AB	30	2.0	-5
.17	$C_6H_5CH_2Cl + [C_6H_5C{:}OCHC_2H_5]^-Na^+ \longrightarrow C_6H_5C{:}OCH(C_2H_5)CH_2C_6H_5 + NaCl$	$(C_2H_5)_2O$	A= 1.7; B=0.13	k AB	30	8.8	-6

COMMENTS

Second order rate constants calculated by dividing pseudo first order constant by concentration of A. Pseudo first order constants increased about 50% during second half life except where α-hydrogen of ketone was substituted. Rate law with respect to A not verified.

LITERATURE

H. D. Zook, W. L. Rellahan, *ACS* 1957, **79**, 881.

EXCHANGE

Replacement of halogen on Si by C

Reaction type: $R'R''R'''S{:}X + R_1MgX' \longrightarrow R'R''R'''SiR_1 + MgXX'$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Comments at end of Table.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$(CH_3)_3SiF + CH_3MgBr \longrightarrow (CH_3)_4Si + MgBrF$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			8.8	1.3	3
.2	$(CH_3)_3SiF + CH_3MgI \longrightarrow (CH_3)_4Si + MgIF$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			13.5	5.0	6
.3	$(CH_3)_3SiCl + CH_3MgCl \longrightarrow (CH_3)_4Si + MgCl_2$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			8.0	1.6	2
.4	$(CH_3)_3SiCl + CH_3MgBr \longrightarrow (CH_3)_4Si + MgBrCl$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			8.1	8	2
.5	$(CH_3)_3SiCl + CH_3MgI \longrightarrow (CH_3)_4Si + MgICl$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			10.6	1.0	5
.6	$(CH_3)_3SiBr + CH_3MgBr \longrightarrow (CH_3)_4Si + MgBr_2$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			10.6	1.0	5
.7	$(CH_3)_3SiBr + CH_3MgI \longrightarrow (CH_3)_4Si + MgIBr$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	-3	1.43	-3			
					5	2.50	-3			
					20	7.55	-3			
					25	1.12	-2	11.3	2.5	6
.8	$(CH_3)_3SiI + CH_3MgI \longrightarrow (CH_3)_4Si + MgI_2$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			9.2	2.0	5
.9	$(ClCH_2)(CH_3)_2SiCl + CH_3MgCl \longrightarrow (ClCH_2)(CH_3)_3Si + MgCl_2$	$(C_2H_5)_2O$	$A = B \simeq 0.25$	k AB	0-25			8.3	8	3

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
						k^o	n		A^o	n
.10	$(ClCH_2)(CH_3)_2SiCl + CH_3MgBr \longrightarrow (ClCH_2)(CH_3)_3Si + MgBrCl$	$(C_2H_5)_2O$	A= B≃0.25	k AB	0-25			11	~8	5
.11	$(ClCH_2)(CH_3)_2SiCl + CH_3MgI \longrightarrow (ClCH_2)(CH_3)_3Si + MgICl$	$(C_2H_5)_2O$	A= B≃0.25	k AB	0-25			9.8	1.6	4

COMMENTS

Rate law with respect to individual reactants not determined as A=B in all experiments. Second order rate law valid until formation of second liquid phase at which point reaction rate observed to increase. At least one half life observed before second phase appeared. Actual rate constants given by authors only for (.7). Values of E and A listed are not known as accurately as given in table. These were not rounded off so that rate constants between 0-25°C may be calculated from them.

LITERATURE

A. F. Reid, C. J. Wilkins, *CSL* **1955**, 4029.

EXCHANGE

Replacement of Halogen by NO_2 and(or) ONO on aliphatic C

Liquid phase

Reaction types: $RX + MNO_2 \longrightarrow RNO_2 + MX$
$\searrow RONO + MX$

Amounts are in M/l. Rate constants are in M/l and sec.
*Coded solvents, Comments, literature, at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$(CH_3)_2CHI + AgNO_2 \longrightarrow (CH_3)_2CHNO_2 + AgI$ (15%) $\longrightarrow (CH_3)_2CHONO + AgI$	$(C_2H_5)_2O$	A= 0.165; B= saturated		0	480						*	(3)
.2	$n\text{-}C_4H_9Br + AgNO_2 \longrightarrow$ $\longrightarrow n\text{-}C_4H_9NO_2,\ n\text{-}C_4H_9ONO + AgBr$	$(C_2H_5)_2O$	A= 0.25; B= saturated		0	1,250,000						*	(4)
.3	$C_2H_5(CH_3)CHBr + AgNO_2 \longrightarrow$ $\longrightarrow C_2H_5(CH_3)CHNO_2, C_2H_5(CH_3)CHONO + AgBr$	$(C_2H_5)_2O$	A= 0.25; B= saturated		0	346,000						*	(4)
.4	$(CH_3)_3CBr + AgNO_2 \longrightarrow$ $\longrightarrow (CH_3)_3CNO_2, (CH_3)_3CONO + AgBr$	$(C_2H_5)_2O$	A= 0.25; B= saturated		0	900						*	(4)
.4.1	$(CH_3)_3CBr + (CH_3)_4NNO_2 \longrightarrow$ $\longrightarrow (CH_3)_3CNO_2, (CH_3)_3CONO + (CH_3)_4NBr$	CH_3NO_2	A= 0.0155; B= 0.032	k A	25 45 63		5.57 5.24 2.90	-6 -5 -4	20.6	7	9	*	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4.2	$(CH_3)_3CBr + (C_2H_5)_4NNO_2 \longrightarrow$	CH_3NO_2	A = 0.020; B = 0.0048	k A	25		3.91	-6				*	(1)
	$\longrightarrow (CH_3)_3CNO_2,\ (CH_3)_3CONO + (C_2H_5)_4NBr$		0.0306		25		5.56	-6					
.5	$n\text{-}C_4H_9I + AgNO_2 \longrightarrow n\text{-}C_4H_9NO_2, n\text{-}C_4H_9ONO + AgI$	$(C_2H_5)_2O$	A = 0.195; B = saturated		0	5,700						*	(4)
		$CH_3C{:}N$	0.16 0.64		0	600							
.6	$C_2H_5(CH_3)CHI + AgNO_2 \longrightarrow$	$(C_2H_5)_2O$	A = 0.195; B = saturated		0	660						*	(4)
	$\longrightarrow C_2H_5(CH_3)CHNO_2 + AgI$ (15%)												
	$\longrightarrow C_2H_5(CH_3)CHONO + AgI$												
.7	$(CH_3)_3CCH_2I + AgNO_2 \longrightarrow$	$(C_2H_5)_2O$	A = 0.195; B = saturated		0	$(t_{0.1} = 2.5 \times 10^6)$						*	(4)
	$\longrightarrow (CH_3)_3CCH_2NO_2,\ (CH_3)_3CCH_2ONO + AgI$				27	940,000							
		$CH_3C{:}N$	A = 0.16; B = 0.64		0	5,800,000							
					~25	330,000							
.8	$n\text{-}C_8H_{17}I + AgNO_2 \longrightarrow$	$(C_2H_5)_2O$	A = 0.195; B = saturated		0	6,550						*	(4)
	$\longrightarrow n\text{-}C_8H_{17}NO_2,\ n\text{-}C_8H_{17}ONO + AgI$												
.9	$(n\text{-}C_6H_{13})(CH_3)CHI + AgNO_2 \longrightarrow$	$(C_2H_5)_2O$	A = 0.195; B = saturated		0	660						*	(4)
	$\longrightarrow (n\text{-}C_6H_{13})(CH_3)CHNO_2 + AgI$ (22%)												
	$\longrightarrow (n\text{-}C_6H_{13})(CH_3)CHONO + AgI$ (16%)												
.10	$C_2H_5OOC(CH_3)CHI + AgNO_2 \longrightarrow$	$(C_2H_5)_2O$	A = 0.165; B = saturated		0	292,000						*	(3)
	$\longrightarrow C_2H_5OOC(CH_3)CHNO_2 + AgI$ (80%)												
	$\longrightarrow C_2H_5OOC(CH_3)CHONO + AgI$												

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No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.11	$CH_3(NO_2)CHCl + NaNO_2 \longrightarrow CH_3CH(NO_2)_2 + NaCl$	Et 50*	A = 0.0114; B = 0.2-0.8	k AB	30		2.75	-4				*	(2)
.12	$CH_3(NO_2)CDCl + NaNO_2 \longrightarrow CH_3CD(NO_2)_2 + NaCl$	Et 50*	A = 0.0114; B = 0.2-0.8	k AB	30		8.5	-5				*	(2)
.13	$C_6H_5CH_2Br + AgNO_2 \longrightarrow$ $\longrightarrow C_6H_5CH_2NO_2 + AgBr$ (70%) $\longrightarrow C_6H_5CH_2ONO + AgBr$ (30%)	$(C_2H_5)_2O$	A = 0.05; B = saturated		0	960						*	(4)
.14	$p\text{-}CH_3C_6H_4CH_2Br + AgNO_2 \longrightarrow$ $\longrightarrow p\text{-}CH_3C_6H_4CH_2NO_2 + AgBr$ (52%) $\longrightarrow p\text{-}CH_3C_6H_4CH_2ONO + AgBr$ (48%)	$(C_2H_5)_2O$	A = 0.05; B = saturated		0	60						*	(4)
.15	$p\text{-}CH_3OC_6H_4CH_2Br + AgNO_2 \longrightarrow$ $\longrightarrow p\text{-}CH_3OC_6H_4CH_2NO_2 + AgBr$ (39%) $\longrightarrow p\text{-}CH_3OC_6H_4CH_2ONO + AgBr$ (61%)	$(C_2H_5)_2O$	A = 0.05; B = saturated		0	very fast						*	(4)
.16	$p\text{-}NO_2C_6H_4CH_2Br + AgNO_2 \longrightarrow$ $\longrightarrow p\text{-}NO_2C_6H_4CH_2NO_2 + AgBr$ (84%) $\longrightarrow p\text{-}NO_2C_6H_4CH_2ONO + AgBr$ (16%)	$(C_2H_5)_2O$	A = 0.05; B = saturated		0	10,800						*	(4)

CODED SOLVENTS

Et 50* 50 vol % $C_2H_5OH + H_2O$

COMMENTS

Reactions: **(.1) (.2) (.3) (.4)** Reaction may be partly or entirely heterogeneous at surface of excess solid $AgNO_2$. **(.4.1) (.4.2)** Rate law followed up to 80% reaction. The nitrite ester formed in the reaction reacts further with Br^- to produce NOBr and $(CH_3)_3COH$. Some elimination to form olefin is also observed. At low concentrations of B rate approaches rate of solvolysis, halogen exchange and many other reactions of $(CH_3)_3CBr$ in this medium. **(.5) (.6) (.7) (.8)** In $(C_2H_5)_2O$ reaction may be partly or entirely heterogeneous at surface of $AgNO_2$. **(.9)** When optically active $(n\text{-}C_6H_{13})(CH_3)CHI$ is used both products, $(n\text{-}C_6H_{13})(CH_3)CHNO_2$ and $(n\text{-}C_6H_{13})(CH_3)CHONO$ are obtained with clean inversion of optical configuration and no appreciable racemization. Percent of products based on actual yields. Reaction may be partly or entirely heterogeneous in this medium. **(.10)** Reaction may be partly or entirely heterogeneous in this medium at surface of excess solid $AgNO_2$. **(.11) (.12)** Pseudo first order up to 80% reaction as B in large excess. Second order constants calculated by dividing pseudo first order constants by concentration of B. Primary isotope effect indicated as ratio is 3.3 showing hydrogen to be involved in rate determining step. Units converted to seconds from original minutes. **(.13) (.14) (.15) (.16)** Percent of products based on titrations and difference, actual percentage yields somewhat lower. Reactions may be partly or entirely heterogeneous at surface of excess solid $AgNO_2$.

LITERATURE

(1) P.B.D. de la Mare, E.D. Hughes, C.K. Ingold, Y. Pocker, *CSL* **1954**, 2930. (2) M.F. Hawthorne, *ACS* 1956, **78**, 4980. (3) N. Kornblum, M.E. Chalmers, R. Daniels, *ACS* 1955, **77**, 6654. (4) N. Kornblum, R.A. Smiley, R.K. Blackwood, D.C. Iffland, *ACS* 1955, **77**, 6269.

EXCHANGE

Replacement of halogen by NO_3^-

Reaction type: $RX + NO_3^-$

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.13	$CH_3Br + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.1; B ≃ 0.14	k AB	64	6.25	-3				*	(1)
.14	$C_2H_5Br + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.1; B ≃ 0.14	k AB	64	7.69	-3				*	(1)
.15	$CH_3CH_2CH_2Cl + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.2; B ≃ 0.5	k AB	95	3.43	-4				*	(1)
.16	$CH_3CH_2CH_2Br + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.1; B ≃ 0.14	k AB	64	4.20	-3				*	(1)
.17	n-$C_4H_9Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	50	2.0	-7				*	(2)
.18	$(CH_3)_2CHCH_2Cl + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.2; B ≃ 0.5	k AB	95	6.34	-5				*	(1)
.19	$(CH_3)_2CHCH_2Br + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.1; B ≃ 0.14	k AB	64	6.44	-4				*	(1)
.20	$(CH_3)_3CCH_2Cl + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.2; B ≃ 0.5	k AB	95	1.59	-5				*	(1)
.21	$(CH_3)_3CCH_2Br + AgNO_3$	C_2H_5OH 70 vol % + H_2O	A ≃ 0.1; B ≃ 0.14	k AB	64	1.01	-4				*	(1)
	Alkenyl halide + nitrate											
.22	$CH_2{:}CHCH_2Cl + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	k AB	25 50	1.73 1.74	-5 -4	18	1	8	*	(3)

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.23	$CH_2{:}CHCH_2Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	50	1.32	-6				*	(2)
.24	$CH_3CH{:}CHCH_2Cl + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	k AB	25	5.56	-3				*	(3)
.25	$CH_2{:}CH(CH_3)CHCl + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	k AB	25	3.25	-3				*	(3)
	Substututed alkyl halides											
.26	$CH_3C{:}OCH_2Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	50	5.2	-8				*	(2)
.27	$C_6H_5OOCCH_2Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	50	5.3	-8				*	(2)
.28	$C_6H_5CH_2Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	20 50	1.40 1.38	-6 -5	14.4	7	4	*	(2)
.29	$C_6H_5C{:}OCH_2Cl + AgNO_3$	C_2H_5OH	A = B = 1.0	k AB	50	1.12	-7				*	(2)
	Di- and Tri-halides											
.30	$CH_3CH_2CH_2CHCl_2 + 2AgNO_3$	C_2H_5OH	A = B = 1.0	$-dB/dt = k$ AB	50	4.3	-8				*	(2)
.31	*cis*-$ClCH{:}CHCH_2Cl + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	$-dB/dt = k$ AB	50	2.48	-4				*	(3)
.32	*trans*-$ClCH{:}CHCH_2Cl + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	$-dB/dt = k$ AB	50	4.31	-4				*	(3)
.33	$CH_2{:}CHCHCl_2 + AgNO_3$	C_2H_5OH	A = 0.5; B = 1.0	$-dB/dt = k$ AB	50	4.22	-4				*	(3)
.34	$C_6H_5CHCl_2 + 2AgNO_3$	C_2H_5OH	A = B = 1.0	$-dB/dt = k$ AB	20	2.56	-5				*	(2)
.35	$C_6H_5CCl_3 + 3AgNO_3$	C_2H_5OH	A = B = 1.0	$-dB/dt = k$ AB	20	5.13	-5				*	(2)

COMMENTS

By Reference: ([1]) consider reactions may be partly heterogeneous at surface of precipitated silver halide but observe good second order behavior from 5 to 50% reaction. ([2]) units converted to seconds from original minutes of authors, who list values as $10^5 k$ which have been interpreted to be $10^{-5} \times k$. ([3]) carry out reaction in the dark to prevent catalytic action of precipitated silver halide.

Reaction: **(.30)** Twice authors value, who divided measured value of $-dB/dt$ by two. Second halogen considered to react very much more rapidly than first. **(.32) (.33)** Identical product obtained from both reactions. **(.34)** Twice value listed by authors. ([2]) divided measured value of $-dB/dt$ by two as second halogen considered to react more rapidly. **(.35)** Three times value listed by authors. ([2]) divided measured value of $-dB/dt$ by three as second and third halogen considered to react more rapidly.

LITERATURE

([1]) I. Dostrovsky, E. D. Hughes, *CSL* **1946**, 169. ([2]) M. Murakami, S. Oae, S. Takeuchi, *Bull. Chem. Soc. Japan* 1951, **24**, 1. ([3]) S. Oae, C. A. Vander Werf, *ACS* 1953, **75**, 2724.

EXCHANGE

Replacement of halogen by azide

Reaction type: $RX + N_3^- \longrightarrow RN_3 + X^-$

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Aryl-substituted Alkyl halide													
.1	$(C_6H_5)_3CCl + (C_{18}H_{38})_2(CH_3)_2NN_3 \longrightarrow$	C_6H_6	$10^2A \simeq 3$; $10^2B = 1.4$			k AB	50	4.5	-2				*	(2)
	$(C_6H_5)_3CN_3 + (C_{18}H_{38})_2(CH_3)_2NCl$		3.0				50	3.3	-2					
			5.4				50	3.6	-2					
			3.0	C_6H_5OH	$(4-8) \times 10^{-3}$	k A[B-(C_6H_5OH)] + k_3A[B-(C_6H_5OH)][C_6H_5OH]								
							50	$k = 3.3$	-2					
							50	$k_3 = 1.6$	+1					
	Aryl halide													
.2	$2\text{-}NO_2C_6H_4I + N_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	132	9.6	-4				*	(1)
							150	3.35	-3					
							158	6.93	-3					
							166	1.05	-2	24.7	2	10		
.3	$2\text{-}NO_2\text{-}4\text{-}O{:}CHC_6H_3I + N_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	52	1.68	-4				*	(1)
							64	6.24	-4					
							82	3.96	-3	24.2	3	12		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.4	$2\text{-}NO_2\text{-}4\text{-}N{:}CC_6H_3I + N_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	45	1.53	-4				*	(1)
							50	2.59	-4					
							66	1.18	-3					
							86	7.6	-3	21.5	1	11		
.5	$2,4\text{-}(NO_2)_2C_6H_3I + N_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	20	1.90	-4				*	(1)
							35	9.13	-4					
							44	2.26	-3					
							59	8.7	-3	19.0	3	10		

COMMENTS

Reaction. **(.1)** In absence of phenol reaction shows good second order behavior over course. In presence of phenol the concentration of phenol must be subtracted from azide concentration to give second order constant as well as a third order catalytic constant involving total phenol concentration. Variation of rate constant with initial concentration of B assumed to be due to variation in size of salt clusters. **(.2) (.3) (.4) (.5)** Rate law is total second order but order not determined with respect to A and B independently as A=B in all experiments.

LITERATURE

(1) J. Miller, A.J. Parker, B.A. Bolto, *ACS* 1957, **79**, 93. (2) C.G. Swain, M.M. Kreevoy, *ACS* 1955, **77**, 1122.

EXCHANGE

Replacement of halogen by NH_2 and :NH

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Reaction type: $CX_4 + 7NH_3 \longrightarrow 4NH_4X + H_2NC(=NH)NH_2$

(A) (B) (L) (M)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$CCl_4 + NH_3$	NH_3	(No appreciable reaction below Tc see 331.754)								
.2	$CBr_4 + 7NH_3 \longrightarrow 4NH_4Br + H_2NC(=NH)NH_2$	NH_3	A = 0.2	L	0-0.25	$dM/dt = k\,AL$	125	4.4	-4	*	
.3	$CI_4 + 7NH_3 \longrightarrow (Q) \longrightarrow 4NH_4I + H_2NC(=NH)NH_2$	NH_3	A = 0.07-0.15	L	0-0.29	$dM/dt = k\,QL'$	125	8.0	-4	*	

COMMENTS

Reactions carried out under pressure slightly below critical temperature. For reactions above critical temperature of NH_3 see 331.754. (.2) Rate law may require alteration after more complete study. Concentrations only estimated at reaction temperature. Formation of Br^- slightly ahead of guanidine formation but results indicate only about 10% of carbon tied up in form of intermediate. Addition of NaBr or KBr at 0.09M/l increase yield in given time by a factor of about four. $BaBr_2$ shows no effect. $CaBr_2$ decreases yield and $AlBr_3$ or $BiBr_3$ at 0.03 M/l show only slight increase in yield in given time. (.3) All I^- appears in first ten minutes of reaction so that carbon is predominantly in form of intermediate, Q. Concentration of Q = A-L/4. Authors show rate of appearance of guanidine is first order with respect to concentration of Q and first order with respect to effective L. Effective L is NH_4I added + $\frac{1}{2}[NH_4I]$ produced by intermediate producing reaction. Rate laws may need to be revised on more complete study. Concentrations only estimated at reaction temperature.

LITERATURE

G.W. Watt, H.T. Hahn, *ACS* 1955, 77, 312.

EXCHANGE

Replacement of halogen by $S_2O_3^=$

Liquid phase

Reaction type: $RX + S_2O_3^= \longrightarrow RS_2O_3^- + X^-$

In compounds with two halogen atoms, if only one is exchanged (reaction with 1 $S_2O_3^=$), it is the one written last. Both halogens are exchanged if the reaction is written with 2 $S_2O_3^=$.

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents at end of table.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.34	.3	$CH_3I + S_2O_3^=$ (Na^+)	Me 10*	$A \simeq B \simeq 0.03$			k AB	25	3.6	-2				*	(20)
			20*					25	4.3	-2					
			50*					25	8.5	-2					
			Pr 10*	$A \simeq B \simeq 0.03$			k AB	25	3.9	-2					
			20*					25	5.8	-2					
			30*					25	6.5	-2					
			50*					25	5.0	-2					
.35	.4	$C_2H_5Br + S_2O_3^=$ (Na^+)	H_2O	$10^2A \simeq 1$; $10^2B \sim 5$			k AB	25	1.19	-3				*	(21)
								50	1.92	-2					
			Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k AB	12	2.98	-4				*	(1)
								25	1.07	-3					
								37	3.33	-3	17.0	3	9		
.36	.5	$C_2H_5I + S_2O_3^=$ (Na^+)	H_2O	$A = B = 0.01$			k AB	25	1.92	-3				*	(21)
								35	6.5	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.37	.11	n-$C_3H_7Br + Na_2S_2O_3$	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	12	1.75	-4				*	(1)
								25	6.31	-4					
								37	1.94	-3	16.9	1.9	9		
			Et 49*	10^4A = 4; 10^4B = 8	CH_3COONa	1.25×10^{-4}	k AB	25	9.44	-4				*	(6)
				8 16		2.5×10^{-4}		25	9.05	-4					
				19 38		5.0×10^{-4}		25	8.29	-4					
				25 60		6.1×10^{-4}		25	7.73	-4					
				111 207		8.4×10^{-4}		25	6.54	-4					
				443 526		5.0×10^{-3}		25	5.73	-4					
				4-400 8-500		$(1\text{-}50) \times 10^{-4}$	k A$[S_2O_3^{=}]$	25	1.02	-3					
.38	.11	n-$C_3H_7Br + K_2S_2O_3$	Et 49*	10^4A = 5; 10^3B = 1	CH_3COONa	1.0×10^{-4}	k AB	25	9.12	-4				*	(6)
				25 5		4.0×10^{-4}		25	7.52	-4					
				443 53		5.0×10^{-3}		25	5.13	-4					
				5-400 1-50		$(1\text{-}50) \times 10^{-4}$	k A$[S_2O_3^{=}]$	25	1.02	-4					
.39	.11	n-$C_3H_7Br + MgS_2O_3$	Et 49*	10^3A $\simeq$ 2; 10^3B = 5	CH_3COONa	$\sim 4 \times 10^{-4}$	k AB	15	1.57	-4				*	(6)
								20	2.64	-4					
								25	4.50	-4					
								30	7.39	-4					
								35	11.14	-4					
				" "	"	"	k A$[S_2O_3^{=}]$	15	3.35	-4					
								20	5.64	-4					
								25	9.62	-4					
								30	1.59	-3					
								35	2.41	-3	18.1	1.5	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.40	.11	n-$C_3H_7Br + CaS_2O_3$	Et 49*	$10^2A = 4$; $10^2B = 5.2$	CH_3COONa	5.0×10^{-3}	k AB	25	3.88	-4				*	(6)
							k A[$S_2O_3^=$]	25	1.04	-3					
.41	.11	n-$C_3H_7Br + SrS_2O_3$	Et 49*	$10^4A = 3$; $10^4B = 6$	CH_3COONa	2×10^{-5}	k AB	25	5.92	-4				*	(6)
				5 10		5×10^{-5}		25	5.35	-4					
				3-5 6-10		$(2\text{-}5) \times 10^{-5}$	k A[$S_2O_3^=$]	25	1.02	-3					
.42	.12	$(CH_3)_2CHBr + Na_2S_2O_3$	Et 49*	$10^5A = 1$; $10^5B = 2$	CH_3COONa	1×10^{-5}	k AB	25	1.8	-5				*	(6) (9)
				1 1		2.5×10^{-5}		25	2.5	-5					
				0.5 1		2×10^{-6}		25	2.94	-5					
				1 2		1×10^{-5}	k A[$S_2O_3^=$]	25	5.0	-5					
				1 1		2.5×10^{-5}		25	5.9	-5					
				0.5 1		2×10^{-6}		25	6.2	-5					
				(extrapolated to $\mu = 0$)				25	7.2	-5					
.43	.13	n-$C_3H_7I + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A = 1$; $B > A$			k AB	35	2.1	-3				*	(21)
.44	.14	$(CH_3)_2CHI + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A = 1$; $B > A$			k AB	35	1.3	-4				*	(21)
.45		n-$C_4H_9Br + S_2O_3^=$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k AB	12	1.32	-4					(1)
								25	4.65	-4					
								37	1.47	-3	16.9	1.1	9		
		Alkenyl halide													
.46		$CH_2{:}CHCH_2Cl + S_2O_3^=$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k AB	12	9.32	-4					(1)
								25	2.51	-3					
								37	7.33	-3	14.5	1.2	8		
.47	.15	$CH_2{:}CHCH_2I + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A = 1$; $B > A$			k AB	15	5.3	-2				*	(21)
								25	1.4	-1					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Alkoxy-substituted alkyl halide															
.48		$C_2H_5OCH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	37	3.44	-4					(1)
								50	1.16	-3					
								62	3.44	-3	19.0	8	9		
.49		$C_2H_5OCH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	25	4.07	-4					(1)
								37	1.36	-3					
								50	4.04	-3	17.6	3	9		
.50		$C_2H_5OCH_2CH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	25	7.26	-4					(1)
								37	2.35	-3					
								50	6.74	-3	17.0	2	9		
Carbonyl-substituted alkyl halide															
.51	.28	$CH_3COCH_2Cl + S_2O_3^{=}$ (Na^+)	H_2O	$10^2A = 1; B > A$			k AB	15	5.1	-3				*	(21)
								25	1.44	-2					
			EtW 3*					25	1.45	-2					
								35	4.0	-2					
Carboxy-substituted alkyl halide															
.52	.17	$C_2H_5OOCCl + S_2O_3^{=}$ (Na^+)	EtW 3*	$10^2A \simeq 1; B > A$			k AB	35	3.9	-2				*	(21)
.53	.18	$(COO^-)CH_2Cl + S_2O_3^{=}$ (Na^+)	H_2O	$10^2A = 1; B > A$			k AB	25	1.6	-4				*	(21)
				A + 2B = 0.02				50	1.30	-3				*	(12)
				0.04				50	1.57	-3				(12)	(21)
				0.08				50	1.77	-3					(12)
				0.15				50	1.96	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.53	.18	$(COO^-)CH_2Cl + S_2O_3^{=}$ (Na^+) *(continued)*	H_2O	$10^2A = 1$; $10^3B = 5$			k AB	60	2.6	-3					(12)
				2 10				60	3.1	-3					
				4 20				60	3.6	-3					
				10 25				60	4.0	-3					
				1 5				70	5.4	-3					
				10 25				70	8.1	-3					
					NaCl	1.11		50	2.6	-3					
.54	.19	$CH_3OOCCH_2Cl + S_2O_3^{=}$ (Na^+)	H_2O	$10^2A \simeq 1$; $B > A$			k AB	25	2.26	-3				*	(21)
								35	6.3	-3					
.55	.20	$C_2H_5OOCCH_2Cl + S_2O_3^{=}$ (Na^+)	H_2O	$10^2A \simeq 1$; $B > A$			k AB	25	2.3	-3				*	(21)
								35	6.6	-3					
.56	.21	$(COO^-)CH_2Br + S_2O_3^{=}$ (Na^+)	H_2O	$A = B = 0.002$			k AB	0	5.17	-4				*	(17)
				0.005				0	5.87	-4					
				0.02				0	8.16	-4					
				0.05				0	1.06	-3					
				0.0008				20	3.33	-3					(10)
				0.004				20	4.23	-3					
				0.0002				25	4.9	-3					(14)
				0.0005				25	5.2	-3					
				0.002				25	5.99	-3					(17)
				0.005				25	7.00	-3					(14) (15) (17) (22)
				0.02				25	9.63	-3					(17) (21)
				0.05				25	1.24	-2					(8) (15) (17)
				0.005				37.5	2.04	-2	16.0	5	9		(17)
				$\mu = 0.00125$				60	3.14	-2					(13)
				0.0050				60	3.80	-2					
				0.020				60	5.55	-2					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.56	.21	$(COO^-)CH_2Br + S_2O_3^=$ (Na^+)	H_2O	μ = 0.00125			k AB	70	6.25	-2				*	(13)
		(continued)		0.0050				70	7.55	-2					
				0.020				70	1.09	-1					
				0.00125				80	1.17	-1					
				0.0050				80	1.42	-1					
				0.020				80	2.05	-1					
				0.00125				90	2.15	-1					
				0.0050				90	2.60	-1					
				0.020				90	3.80	-1	15.7				
				A = B = (2-50) × 10^{-4}			k AB; $\log k = \log k_o + 1.62\sqrt{\mu}/(1+\sqrt{\mu})$								(14)
								25	k_o = 4.30	-3					
				(2.5-50) × 10^{-4}	NaCl	(5-1500) × 10^{-5}	k AB; $\log k = \log k_o + 1.62\sqrt{\mu}/(1+\sqrt{\mu})$								
								25	k_o = 4.35	-3					
				(2.5-50) × 10^{-4}	$LaCl_3$	(5-5000) × 10^{-6}	k AB; $k = k' + k''[LaCl_3]$								
			H_2O	A = B = 0.047	pressure	1 atm.	k AB	25	1.08	-2				*	(8)
						340		25	1.14	-2					
						680		25	1.25	-2					
						1,260		25	1.37	-2					
.57	.22	$CH_3OOCCH_2Br + S_2O_3^=$ (Na^+)	H_2O	$10^2A \simeq 1$; B > A			k AB	15	8.0	-2				*	(21)
								25	2.2	-1					(21) (16)
				A = B = 0.0026	pressure	1 atm.		25	1.46	-1					(8)
						680		25	1.30	-1					
						1,220		25	1.26	-1					
.58	.23	$C_2H_5OOCCH_2Br + S_2O_3^=$ (Na^+)	H_2O	$10^2A \simeq 1$; B > A			k AB	15	9.0	-2				*	(21)
								25	2.5	-1					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.59	.24	$C_2H_5OOCCH_2I + S_2O_3^{=}$ (Na^+)	H_2O	$10^2A \simeq 1; B > A$			k AB	15	9.8	-2				*	(21)
								25	2.8	-1					
.60		$(COO^-)CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	H_2O	$10^3A = 1\text{-}30;$		$\mu = 0.28$	k AB	25	2.65	-4					(16)
				$10^3B = 2\text{-}70$		0.06		25	3.60	-4					
						0.009		25	1.4	-3					
						0.006		25	2.35	-3					
.61		$CH_3OOCCH_2CH_2Br + S_2O_3^{=}$ (Na^+)	H_2O	$10^3A = 4.5$		$\mu = 0.21$	k AB	25	5.0	-4					(16)
				2.0		0.21		25	6.4	-4					
				1-2.2		0.005-.5		25	5.0	-4					
.62		$(COO^-)(CH_3)CHBr + S_2O_3^{=}$ (Na^+)	H_2O	$10^3A = 3\text{-}30;$		$\mu = 0.008$	k AB	25	4.40	-5					(16)
				$10^3B = 7\text{-}70$		0.03		25	6.25	-5					
						0.06		25	7.2	-5					
						0.25		25	8.3	-5					
.63		$(CH_3OOC)(CH_3)CHBr + S_2O_3^{=}$ (Na^+)	H_2O	$10^3A = 3$		$\mu = 0.16$	k AB	25	2.8	-3					(16)
						0.09		25	3.0	-3					
						0.02		25	3.7	-3					
						0.005		25	3.6	-3					
.64	.25	$(C_2H_5OOC)(CH_3)CHBr + S_2O_3^{=}$ (Na^+)	EtW 3*	$10^2A \simeq 1; B > A$			k AB	25	1.4	-3				*	(21)
								35	3.2	-3					
.65	.26	$(C_2H_5OOC)(C_2H_5)CHBr + S_2O_3^{=}$ (Na^+)	EtW 3*	$10^2A \simeq 1; B > A$			k AB	35	8.5	-4				*	(21)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
		Dicarboxy-substituted alkyl halide													
.66		$(COO^-)_2CHBr + S_2O_3^=$ (Na^+)	H_2O	$10^3A \simeq 4$; $10^3B \simeq 8$		$\mu = 0.08$	k AB	0	9.2	-6				*	(4)
						0.04		0	1.29	-5					
						0.025		0	2.52	-5					
						0.014		0	5.48	-5					
				$10^2A \simeq 1$;		0.46		25	3	-5					(5)
				$10^2B = 3$-6		0.41		25	6	-5					
						0.3		25	1.0	-4					
						0.15		25	1.5	-4					
			MD 78*	A = B = 0.01				25	3.5	-5					(2)
			71*					25	5.7	-5					
			63*					25	9.3	-5					
			54*					25	1.65	-4					
			44*					25	2.24	-4					
			71*					45	3.78	-4					
			64*					45	5.30	-4					
			56*					45	8.1	-4					
			43*					45	1.42	-3					
.67		$(C_2H_5OOC)_2CHBr + S_2O_3^=$	MD 71*	A = B = 0.01			k AB	0	9.74	-4				*	(7)
			54*					0	3.94	-1					
			46*					0	2.00	-1					
			69*					25	6.55	0	12.1	4	9		
			51*					25	2.34	0	13	1	10		
			41*					25	1.20	0	14.4	7	7		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.68		$(COO^-)(^-OOCCH_2)CHBr + S_2O_3^=$	H_2O	$10^3A \simeq 4$; $10^3 \simeq 8$		$\mu = 0.0046$	k AB	0	6.8	-4				*	(4)
						0.02		0	6.5	-5					
						0.05		0	3.0	-5					
						0.10		0	2.3	-5					
				$10^2A \simeq 1$; $10^2B = 3$-6		0.08		25	6.04	-3					(5)
						0.15		25	1.98	-3					
						0.35		25	9.0	-4					
						0.51		25	4.7	-4					
				$10^3A \simeq 4$; $10^3B \simeq 8$		0.04		35	5.6	-3	24	7	14		(4)
						0.05		35	5.4	-3	25	2	15		
.69		$(CH_3OOC)(CH_3OOCCH_2)CHBr + S_2O_3^=$		$10^2A \simeq 1$; $10^2B = 3$-6		$\mu = 0.12$		25	1.34	-3				*	(5)
						0.23		25	1.29	-3					
						0.39		25	1.24	-3					
		Aryl-substituted alkyl halide													
.70	.30	$C_6H_5CH_2Cl + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A \simeq 1$; $B > A$			k AB	35	6.5	-3				*	(21)
			Et 60*	$10^2A \simeq 2$; $10^2B \simeq 4$				30	5.35	-3					(11)
			DMD*	$10^2A \simeq 2$; $10^2B \simeq 4$				30	7.10	-3					
.71		p-$(CH_3)_2CHC_6H_4CH_2Cl + S_2O_3^=$ (Na^+)	Et 60*	$10^2A \simeq 2$; $10^2B \simeq 4$			k AB	30	8.35	-3				*	(11)
			DMD*					30	7.95	-3					
.72	.31	o-$NO_2C_6H_4CH_2Cl + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A \simeq 1$; $B > A$			k AB	35	6.5	-3				*	(21)
.73	.32	m-$NO_2C_6H_4CH_2Cl + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A \simeq 1$; $B > A$			k AB	35	7.4	-3				*	(21)
.74	.33	p-$NO_2C_6H_4CH_2Cl + S_2O_3^=$ (Na^+)	EtW 3*	$10^2A \simeq 1$; $B > A$			k AB	35	1.2	-2				*	(21)
			Et 60*	$10^2A \simeq 2$; $10^2B \simeq 4$				30	9.6	-3					(11)
			DMD*	2 4				30	2.60	-2					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.75		p-$ClC_6H_4CH_2Cl + S_2O_3^{=}$ (Na^+)	Et 60*	$10^2A \simeq 2$; $10^2B \simeq 4$			k AB	30	7.3	-3				*	(11)
			DMD*	2 4				30	1.20	-2					
.76		$C_6H_5CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	37	8.9	-4					(1)
								50	3.24	-3					
								62	8.5	-3	17.9	4	9		
.77		$C_6H_5CH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	25	4.17	-4					(1)
								37	1.53	-3					
								50	4.65	-3	17.9	6	9		
.78		$C_6H_5CH_2CH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	37	1.36	-3					(1)
								50	4.34	-3					
								62	1.28	-2	17.8	5	9		
Sulfonyl-substituted alkyl (alkenyl) halides															
.79		$C_2H_5SO_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	25	7.22	-4					(1)
								37	2.60	-3					
								50	8.1	-3	19.2	8	10		
.80		$C_2H_5SO_2CH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	25	3.58	-3					(1)
								37	1.23	-2					
								50	3.33	-2	17.2	1.4	10		
.81		$C_2H_5SO_2CH{:}CHCH_2Cl + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	12	1.71	-3					(1)
								25	5.36	-3					
								37	1.80	-2	15.8	2	9		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
		Halogen-substituted alkyl halide													
.82	.6	$CH_2ClCH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	*k* AB	25	1.07	-4					(1)
								37	3.76	-4					
								50	1.26	-3	18.3	3	9		
			EtW 3*	B > A				40	1.9	-5				*	(21)
								50	5.8	-5					
.83	.7	$CH_2ClCH_2I + S_2O_3^{=}$ (Na^+)	EtW 3*	B > A			*k* AB	40	5.3	-5				*	(21)
								50	1.5	-4					
.84	.8	$CH_2BrCH_2Br + S_2O_3^{=}$ (Na^+)	EtW 3*	B > A			*k* AB	40	6.4	-3				*	(21)
								50	1.9	-2					
.85	.9	$CH_2BrCH_2I + 2S_2O_3^{=}$ (Na^+)	EtW 2*	A≃0.01; B > A			*k* AB	15	8.1	-3				*	(21)
								25	2.1	-2					
.86	.10	$CH_2ICH_2I + 2S_2O_3^{=}$ (Na^+)	EtW 2*	A≃0.01; B > A			*k* AB	15	1.3	-2				*	(21)
								25	3.9	-2					
.87		$ClCH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	*k* AB	25	4.05	-4					(1)
								37	1.35	-3					
								50	4.26	-3	17.4	2	9		
.88		$ClCH_2CH_2CH_2CH_2Br + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	*k* AB	12	1.97	-4					(1)
								25	7.34	-4					
								37	2.33	-3	16.6	1.1	9		
.89		*cis*-$ClCH{:}CHCH_2Cl + S_2O_3^{=}$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	*k* AB	12	2.59	-3					(1)
								25	7.42	-3					
								37	2.16	-2	14.4	3	8		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.90		*trans*-ClCH:CHCH$_2$Cl + $S_2O_3^=$ (Na^+)	Et 50*	A = B = 0.1	CH_3COONa	0.01	k AB	12	1.60	-3					(1)
								25	4.84	-3					
								37	1.37	-2	14.5	2	8		
.91		O(CH_2CH_2Cl)$_2$ + 2$S_2O_3^=$ (Na^+)	H_2O	A≃0.02; B=0.05-0.1			k AB	100	~ 5	-3					(3)

CODED SOLVENTS

Me 10* (20) (30)	$CH_3OH + H_2O$ % indicated of CH_3OH
Pr 10* (20) (30) (50)	$(CH_3)_2CHOH + H_2O$ % indicated of $(CH_3)_2CHOH$
Et 50* (49) (60)	$H_2O + C_2H_5OH$ % indicated of C_2H_5OH
EtW 2*	$C_2H_5OH + H_2O$; C_2H_5OH/H_2O = 5/2 (vol)
EtW 3*	$C_2H_5OH + H_2O$; C_2H_5OH/H_2O = 5/3 (vol)
MD 78* (71) (64) (63) (56) (54) (44) (43)	$CH_3OH + H_2O$ in ratio necessary to give dielectric constant of value indicated.
DMD*	60 vol % $(CH_3OC_2H_4)_2O + H_2O$

Supplement 1958

COMMENTS

Reaction: **(.34)** Units converted to M/l, sec. and natural logarithms from ml. of titrating solution, min. and base 10 logarithms respectively. **(.35)** Rate constant converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. **(.36)** Rate constant converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. Values about 50% higher than values of ([17]). **(.37)** Values of ([1]) of rate constants 30 to 40% higher than those of ([17]). ([6]) determine fraction of total thiosulfate present as $S_2O_3^{=}$ and find rate constant in terms of true $[S_2O_3^{=}]$ is independent of added salt, see (.38) (.39) (.40) (.41). **(.38) (.39) (.40) (.41)** Rate constant calculated on basis of total thiosulfate present decreases both with course of reaction, and with increase in concentration of salts. In terms of calculated $[S_2O_3^{=}]$ the rate constant is independent of cation present. **(.42)** Data of ([9]) converted into terms of calculated concentration of $[S_2O_3^{=}]$ by ([6]). **(.43) (.44) (.47) (.51) (.52)** Converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. **(.53)** Converted to base e logarithms from base 10 logarithms of ([21]) and from assumed base 10 logarithms of ([12]). **(.54) (.55)** Converted to base e logarithms from base 10 of authors and from values in 1951 Edition of Tables. **(.56)** Reaction studied by ([8]) with regard to pressure dependence from which they concluded the volume of the transition state to be smaller than the volume of the reactants. ([10]) determined dependence with respect to ionic strength:

$$\log k = \log k_o + 2\sqrt{\mu} \text{ and at } 20^\circ C \quad 10^3 k_o = 2.54.$$

Give plot of data of many previous investigators. ([12]) ([13]) determine temperature dependence of reaction. ([14]) studied reaction over wide range of salt concentrations and observed a specific catalytic effect with $LaCl_3$. Catalytic constant for $LaCl_3$ varied with concentration as did activation energy. ([15]) ([16]) ([17]) studied effect on reaction of a wide variety of salts as well as other addends. $\log (k/k_o)/2\sqrt{\mu}$ was not constant but observed to vary from 0.6 at $\sqrt{\mu} = 0.36$ with K^+ or Na^+ to 5.7 at $\sqrt{\mu} = 0.08$ with La^{+++}. Other addends included, urea, sucrose, glycerol and dioxane. ([19]) studied reaction with respect to KNO_2, K_2SO_4, $K_3Co(CN)_6$ and found rate constant to be nearly the same for 0.02N salts even though μ varied from 0.02 to 0.04. Rate constants of ([21]) converted to base e logarithm from base 10 of authors. Reaction also studied by ([23]) ([24]) whose results agree well with those of later investigators. **(.57)** Values of ([21]) converted to base e loga-

COMMENTS *(continued)*

rithms from base 10 as in 1951 edition of Tables. ([8]) shows that pressure dependence indicates transition state to have greater volume than volume of reactants. **(.58) (.59) (.64) (.65)** Converted to base e logarithms from base 10 used by authors and from values in 1951 Edition of Tables. **(.66)** Values of rate constants of ([2]) do not apply to initial stages of reaction. Initial rate may be as much as double steady value obtained as reaction proceeds. ([4]) do not give concentrations of reactants used, and reaction followed for only 20%. Values of ([5]) give only order of magnitude as calculated constants show wide variation. **(.67)** Selected data. Authors attempt to correlate variation of rate constants with dielectric constant of medium by equation of one of the authors. Addition of KNO_3 at constant solvent composition shows very slight negative salt effect. **(.68)** Selected data. Reaction followed to only 20% completion and concentration of reactants and added salts, if any, not stated. **(.69)** Selected data. Ionic strength as listed is initial value. **(.70)** Rate constant converted to base e logarithms from base 10 of ([21]) and from value in 1951 edition of Tables. Solvent composition of ([11]) not exact as no correction for contraction on mixing. **(.71)** No correction for contraction of solvent on mixing. **(.72) (.73)** Rate constants converted to base e logarithms from base 10 of authors and from values in 1951 Edition of Tables. **(.74)** Rate constant converted to base e logarithms from base 10 of ([21]) and from value in 1951 Edition of Tables. No correction made by ([11]) for solvent contraction on mixing. **(.75)** No correction made for contraction of solvent on mixing. **(.82) (.83) (.84) (.85) (.86)** Rate constants converted to base e logarithms from base 10 of ([21]) and from values in 1951 Edition of Tables.

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EXCHANGE

Replacement of halogen by Thio alkyl (aryl)

Reaction type: $RX + R'S^- \longrightarrow RSR' + X^-$

Amounts are in M/l. Rate constants are in M/l and sec.

* Coded solvents at end of Table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C_2H_5Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 1\text{-}4$			k AB	0	3.79	-4					([8])
							20	3.91	-3					
							35	1.82	-2	18.7	3	11		
.2	$C_2H_5Br + C_6H_5\text{-}N(C{:}O\text{-}NH)\text{-}N{=}CS^-$ (Na^+) (sodium 3-phenyl-1-thiourazolate)	Et 50*				k AB	25	1.95	-3				*	([1]) ([3])
.3	$C_2H_5I + C_6H_5\text{-}N(C{:}O\text{-}NH)\text{-}N{=}CS^-$ (Na^+) (sodium 3-phenyl-1-thiourazolate)	Et 50*				k AB	25	6.0	-3				*	([1]) ([3])
.4	$CH_3CH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$			k AB	0	2.56	-4					([8])
							20	2.56	-3					
							35	1.12	-2	18.3	1.1	11		
.5	$CH_3CH_2CH_2Br + C_6H_5\text{-}N(C{:}O\text{-}NH)\text{-}N{=}CS^-$ (Na^+) (sodium 3-phenyl-1-thiourazolate)	Et 50*				k AB	25	1.27	-3				*	([1]) ([3])

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6	$CH_3CH_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 1$; $10^2B = 2.4$			k AB	0	1.47	-3					(8)
							20	1.28	-2	17.3	1.0	11		
.7	$CH_3CH_2CH_2I + C_6H_5-N(C{:}O-NH)-N=CS^-$ (Na^+) (sodium 3-phenyl-1-thiourazolate)	Et 50*				k AB	25	3.33	-3				*	(1) (3)
.8	$n\text{-}C_4H_9Br + n\text{-}C_4H_9S^-$ (Na^+)	CH_3OH	A = B = 0.01			k AB	25	4.43	-3				*	(9)
							35	1.11	-2					
							42	2.00	-2	17.1	2	8		
		C_2H_5OH	A = B = 0.05			k AB	25	2.00	-2					(9)
			0.1				25	1.81	-2					
			0.2				25	1.83	-2					
			0.05				35	5.10	-2					
			0.1				35	4.84	-2					
			0.2				35	4.50	-2					
			0.05	LiCl	0.020		35	4.87	-2					
			0.05		0.033		35	4.78	-2					
			0.05		0.046		35	4.48	-2					
			0.05		0.068		35	4.35	-2					
			0.05	C_6H_5ONa	0.084		35	5.0	-2					
			0.05				42	8.94	-2	17	1	9		
			0.1				42	8.84	-2	17.5	2	9		
			0.2				42	7.58	-2	16	9	8		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.9	$n\text{-}C_4H_9Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$			k AB	0	2.77	-4				*	(7)
							20	2.69	-3					
			A = B = 0.1				25	4.43	-3					(9)
			$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$				35	1.21	-2	17.7	4	10		(7)
			A = B = 0.1				35	1.11	-2					(9)
							42	2.00	-2					
		C_2H_5OH	A = B = 0.05			k AB	25	1.28	-2				*	(9)
			0.10				25	1.25	-2					
			0.20				25	1.24	-2					
			0.05				35	3.42	-2					
			0.10				35	3.12	-2					
			0.20				35	2.84	-2					
			0.05				42	6.57	-2	17.4	8	10		
			0.10				42	5.54	-2	15.7	4	9		
			0.20				42	4.75	-2	14.1	3	8		
.10	$n\text{-}C_6H_{13}Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B = 2.4$			k AB	0	3.14	-4					(8)
							29	7.78	-3	18	8	10		
	Halogen-substituted alkyl halide													
.11	$ClCH_2Cl + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k$ AB	20	4.28	-6				*	(8)
							40	4.44	-5	22	1.0	11		
.12	$FCH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			k AB	0	1.98	-4				*	(8)
							40	1.52	-2	18.5	1.3	11		
.13	$ClCH_2Br + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k$ AB	0	2.28	-5				*	(8)
							40	2.51	-3	20.0	2	11		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.14	$BrCH_2Br + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k\,AB$	0	7.98	-6				*	(8)
							40	1.00	-3	20.6	2	11		
.15	$FCH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$k\,AB$	0	4.79	-3				*	(8)
							30	9.64	-2	16.5	8	10		
.16	$ClCH_2I + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k\,AB$	0	1.83	-4				*	(8)
							40	1.49	-2	18.7	1.8	11		
.17	$BrCH_2I + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k\,AB$	0	8.11	-5				*	(8)
							40	7.98	-3	19.5	3	11		
.18	$ICH_2I + 2C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \simeq 1$; $10^2B \simeq 2.4$			$-dA/dt = k\,AB$	0	2.38	-4				*	(8)
							40	2.16	-2	19.2	6	11		
.19	$FCH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$			$k\,AB$	0	4.03	-5				*	(7)
							20	4.95	-4					
							35	2.55	-3	20.0	4	11		
.20	$ClCH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$			$k\,AB$	0	4.86	-5				*	(7)
							20	5.61	-4					
							35	2.85	-3	19.7	3	11		
.21	$BrCH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 2\text{-}9$; $10^2B = 2\text{-}4$			$k\,AB$	0	4.5	-5				*	(7)
							20	5.0	-4					
							35	2.43	-3	19.3	1.2	11		
.22	$FCH_2CH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 1$; $10^2B = 2.4$			$k\,AB$	0	1.86	-4				*	(8)
							29	5.26	-3	18.7	2	11		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.23	$ClCH_2CH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	2.54	-4				*	(8)
							29	7.06	-3	18.6	2	11		
.24	$BrCH_2CH_2CH_2Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $B \ll A$			k AB	0	5.78	-4				*	(8)
							20	5.98	-3	18.7	5	11		
.25	$FCH_2CH_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	1.12	-3				*	(8)
							20	1.04	-2	17.8	2	11		
.26	$ClCH_2CH_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	1.57	-3				*	(8)
							20	1.38	-2	17.4	1.3	11		
.27	$BrCH_2CH_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	2.18	-3				*	(8)
							20	1.91	-2	17.4	2	11		
.28	$ICH_2CH_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $B \ll A$			k AB	0	4.02	-3				*	(8)
							20	3.62	-2	17.6	5	11		
.29	$ClCH_2(CH_2)_2CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	2.39	-3				*	(8)
							20	2.04	-2	17.2	1.4	11		
.30	$ClCH_2(CH_2)_3CH_2I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A \sim 1$; $10^2B \simeq 2.4$			k AB	0	2.29	-3				*	(8)
							20	1.95	-2	17.1	1.2	11		
	Halogen-substituted alkenyl halide													
.31	*cis*-$ClCH{:}CHCl + 2p\text{-}CH_3C_6H_4S^-$ (Na^+)	C_2H_5OH	A = 0.13; B = 0.20	C_2H_5ONa	0.04-0.3	$-dA/dt = k\,A[C_2H_5ONa]$	57	1.27	-4	34	4	18	*	(11)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Mono-substituted Aryl halide													
.32	p-$NO_2C_6H_4F + C_6H_5S^-$ (Na^+)	CH_3OH	$10^2A = 3$; $10^2B = 6.4$			k AB	35	5.01	-4					(2)
							50	2.17	-3					
							60	5.67	-3	19.8	5	10		
.33	o-$NO_2C_6H_4Cl + C_6H_5S^-$ (Na^+)	D1W60*	A = B = 0.015			k AB	25	7.7	-5				*	(6)
.34	p-$NO_2C_6H_4Cl + C_6H_5S^-$ (Na^+)	D1W60*	A = B = 0.015			k AB	25	4.5	-4				*	(6)
	Di-substituted Aryl halide													
.35	$2,4$-$(NO_2)_2C_6H_3F + C_6H_5S^-$ (Na^+)	CH_3OH	$10^4A = 10^4B = 9$			k AB	0	1.03	+2					(5)
.36	$2,4$-$(NO_2)_2C_6H_3Cl + C_6H_5S^-$ (Na^+)	CH_3OH	$10^3A = 10^3B = 4$-9			k AB	0	3.89	0					(5)
							8	6.4	0					
							15	1.05	+1					
.37	2-NO_2-4-$ClC_6H_3Cl + C_6H_5S^-$ (Na^+)	D1W60*	A = B = 0.015			k AB	25	3.0	-3				*	(4) (6)
.38	2-NO_2-4-$F_3CC_6H_3Cl + C_6H_5S^-$ (Na^+)	D1W60*	A = B = 0.015			k AB	0	4.37	-2					(4)
							25	2.26	-1	10.6	1.4	7		
.39	$2,4$-$(NO_2)_2C_6H_3Br + C_6H_5S^-$ (Na^+)	CH_3OH	$10^3A = 10^3B = 4$-9			k AB	0	6.7	0					(5)
							8	1.1	+1					
							15	1.7	+1	9.8	5	8		
.40	$2,4$-$(NO_2)_2C_6H_3I + C_6H_5S^-$ (Na^+)	CH_3OH	$10^3A = 10^3B = 4$			k AB	0	5.2	0					(5)
							8	9.3	0					
							15	1.4	+1	10.7	2	9		

Supplement 1958

SOLVENTS

Et 50*	C_2H_5OH 50 % + H_2O
DiW 60*	60 vol % dioxane + 40 vol % H_2O

COMMENTS

Literature: (7) (8) $\Delta H^{\ddagger}$ of authors converted to E by adding RT for purpose of comparison.

Reaction: (.2) (.3) (.5) (.7) Structure presented for B is the enolate form favored by (1). (.8) (.9) Reaction followed to about 53%. Parallel solvolysis reaction probably negligible, see 212.471 (.193). Decrease of rate constants with increase in concentration of reactants is of the same order of magnitude as that caused by addition of a neutral salt. Plot of log *k* values of (7) (9) versus 1/T gave a good straight line from which an average activation energy was determined. (.11) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.12) Rate constant calculated on basis of only Br being replaced. (.13) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.14) Rate constant calculated on basis of second bromine reacting rapidly after replacement of first. Value tabulated is observed rate which is two times the value per halogen of the authors. (.15) Rate constant calculated on basis of only iodine being replaced. (.16) (.17) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.18) Rate constant calculated on basis of second iodine reacting rapidly after replacement of first. Value tabulated is observed rate which is two times the value per halogen listed by the authors. (.19) (.20) Rate constant calculated on the basis of only bromine being replaced. Slight upward drift of rate constant, observed with chloride, eliminated by using excess alkyl halide. (.21) Calculated second order rate constants drift upward due to participation of second bromine. Value tabulated is initial rate obtained by graphical extrapolation to zero time. (.22) (.23) Rate constant calculated on the basis of only bromine being replaced. Second halogen probably contributes very slightly to overall rate constant. (.25) Rate constant calculated on basis of only one bromine reacting as A in large excess. Values tabulated are observed values, or two times the value per halogen listed by authors. (.25) (.26) (.27) Rate constant calculated on the basis

COMMENTS *(continued)*

of only iodine being replaced. Second halogen probably contributes very slightly to overall rate constant. **(.28)** Rate constant calculated on basis of only one iodine reacting as A in large excess. Values tabulated are observed values, or two times the value per halogen listed by authors. **(.29) (.30)** Rate constant calculated on the basis of only iodine being replaced. Second halogen probably contributes very slightly to overall rate constant. **(.31)** Pseudo first order rate law with respect to A. Second order constant calculated by dividing by the C_2H_5ONa concentration. Authors postulate reaction involves direct elimination of HCl follow by rapid addition to give the dithioalkenylether. High value of "A-factor" probably indicates that this is not the complete rate equation. Reaction deviates from pseudo first order behavior at low concentrations of B. **(.33)** Spectrophotometric method. "Infinity" samples indicated only 42% of the theoretical amount of sulfide formed. **(.34)** Value is the average between the spectrophotometric method (higher) and analytical method for following reaction. "Infinity" samples indicated only 69% of the theoretical amount of sulfide formed. **(.37)** Value is a mean of results of (4) (6). Spectrophotometric method appears to give higher values.

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EXCHANGE

Replacement of halogen by thiocyanate

Reaction type: $RX + SCN^- \longrightarrow RSCN + X^-$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	C_2H_5Br + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.67	-5					(1)
.2	n-C_3H_7Br + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.15	-5					(1)
.3	n-C_4H_9Br + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.14	-5					(1)
.4	$(CH_3)_2CHCH_2Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	5	-7					(1)
.5	n-$C_5H_{11}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.20	-5					(1)
.6	$(CH_3)_2CHCH_2CH_2Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	7.3	-6					(1)
.7	n-$C_6H_{13}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.22	-5					(1)
.8	$(CH_3)_2CHCH_2CH_2CH_2Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.23	-5					(1)
.9	n-$C_7H_{15}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.24	-5					(1)
.10	n-$C_8H_{17}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.27	-5					(1)
.11	n-$C_{10}H_{21}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.23	-5					(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.12	n-$C_{16}H_{33}Br$ + NaSCN	95% C_2H_5OH	A = 0.09; B = 0.2	k AB	25	1.20	-5					(1)
	Aryl halide											
.13	2-NO_2-4-HC:OC_6H_3I + KSCN	CH_3OH	A = B = 0.05	k AB	100	2.41	-4				*	(2)
					111	5.61	-4					
					132	2.38	-3	21.8	1.6	9		
.14	2-NO_2-4-CH_3C:OC_6H_3I + KSCN	CH_3OH	A = B = 0.05	k AB	111	2.20	-4				*	(2)
					131	9.06	-4					
					138	1.39	-3	21.3	3	8		
.15	2-NO_2-4-N:CC_6H_3I + KSCN	CH_3OH	A = B = 0.05	k AB	82	9.8	-5				*	(2)
					100	3.88	-4					
					131	3.70	-3	21.2	1.0	9		
.16	2,4-$(NO_2)_2C_6H_3I$ + KSCN	CH_3OH	A = B = 0.05	k AB	60	1.32	-4				*	(2)
					82	8.42	-4					
					100	3.31	-3	20.0	2	9		

COMMENTS

Reactions: **(.13) (.14) (.15) (.16)** Produce in addition to thiocyanates, diarylsulfides and some disulfides.

LITERATURE

(1) T. I. Crowell, *ACS* 1953, **75**, 6046. (2) J. Miller, A.J. Parker, B.A. Bolto, *ACS* 1957, **79**, 93.

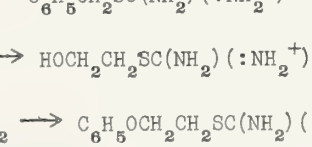
EXCHANGE

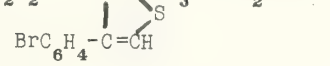
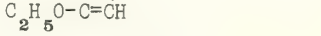
Replacement of halogen by S of thiourea

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Reaction type: $RX + S:C(NH_2)_2 \longrightarrow RSC(NH_2)(:NH_2^+) + X^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
.1	$(CH_3)_2C:CHCH_2Cl + S:C(NH_2)_2 \longrightarrow (CH_3)_2C:CHCH_2SC(NH_2)(:NH_2^+) + Cl^-$	$(CH_3)_2CO$	$10^2A=2$; $10^2B=7$	kAB	45	5.3	-4				(2)
					75	3.3	-3	14	1.4	6	
.2	$CH_2:CH(CH_3)_2CCl + S:C(NH_2)_2 \longrightarrow CH_2:CH(CH_3)_2CSC(NH_2)(:NH_2^+) + Cl^-$	$(CH_3)_2CO$	$10^3A=3-30$; $10^2B=7$	kAB	45	2.56	-5				(2)
					75	3.22	-4	19	1.8	8	
.3	$CH_3CH_2Br + S:C(NH_2)_2 \longrightarrow CH_3CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	7.2	-5				(1)
.4	$CH_3CH_2CH_2Br + S:C(NH_2)_2 \longrightarrow CH_3CH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	4.7	-5				(1)
.5	$CH_2:CHCH_2Br + S:C(NH_2)_2 \longrightarrow CH_2:CHCH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	5.5	-3				(1)
.6	$C_6H_5CH_2Br + S=C(NH_2)_2 \longrightarrow C_6H_5CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	1.40	-2				(1)
.7	$HOCH_2CH_2Br + S=C(NH_2)_2 \longrightarrow HOCH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	8.0	-6				(1)
.8	$C_6H_5OCH_2CH_2Br + S=C(NH_2)_2 \longrightarrow C_6H_5OCH_2CH_2SC(NH_2)(:NH_2+) + Br^-$	CH_3OH		kAB	35	8.8	-6				(1)
.9	$C_6H_5C:OCH_2Br + S=C(NH_2)_2 \longrightarrow$  $+ H_2O + Br^-$	CH_3OH	$10^2A=10^2B=2-5$	kAB	0	4.3	-2			*	(1)
			$10^3A=8.7$; $10^2B=2.6$		0	3.5	-2				
			8.5 15		0	3.2	-2				
			3.5 13.5		0	2.9	-2				

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
.10	$2,4,6\text{-}(CH_3)_3C_6H_2C{:}OCH_2Br + S{=}C(NH_2)_2 \longrightarrow 2,4,6\text{-}(CH_3)_3C_6H_2C{:}OCH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		kAB	35	6.7	-4				([1])
.11	$BrC_6H_4C{:}OCH_2Br + S{=}C(NH_2)_2 \longrightarrow$  $+ H_2O + Br^-$	CH_3OH		kAB	35	7.7	-1				([1])
.12	$C_2H_5OOCCH_2Br + S{=}C(NH_2)_2 \longrightarrow$  $+ H_2O + Br^-$	CH_3OH		kAB	35	3.0	-2				([1])

COMMENTS

No measurable reaction observed with fully substituted thioureas. Reaction (.9) addition of H_2O at 1 M or p-$CH_3C_6H_4SO_3H$ at 0.025 M caused no measurable change in rate of reaction. Addition of .007 M KBr may have increased rate slightly.

LITERATURE

([1]) R.G. Pearson, S.H. Langer, F.V. Williams, W.J. McGuire, *ACS* 1952, **74**, 5130.

([2]) J.M. Rule, I.J. Wilk, T.I. Wriglely, W.G. Young, *ACS* 1957, **79**, 6529.

EXCHANGE

Halogen for halogen on aliphatic carbon

Reaction types: $RX + X'^{-} \longrightarrow RX' + X^{-}$

$RX + X'X'' \longrightarrow RX' + XX''$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Coded solvents at end of table.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	$A = A^{o} \times 10^{n}$ A^{o}	n	Comments	Literature
.71		$CH_3Br + Cl^-$	$(CH_3)_2CO$	A = 0.12; B = 0.05	Li^+	= B	k AB	0.0	5.20	-4				*	(29)
								12.0	1.75	-3					
								24.8	5.92	-3					
								34.0	1.29	-2	15.7	2	9		
.72	.1	$CH_3Br + I^-$	$(CH_2OH)_2$	10^2A = 4-5; 10^2B = 3-10			k AB	15	1.13	-3				*	(37)
				4 3-5				25	3.28	-3					
				4 10				25	2.90	-3					
				4 4				35	8.76	-3					
				4 4				45	2.17	-2	17.9	5	10		
			$(CH_3)_2CO$	10^2A = 4; 10^2B = 2	Li^+	= B	k AB	-11	5.82	-3					(18)
								0	2.19	-2					(18) (39)
								10	6.15	-2	16.3	2	9		
					Na^+ or K^+	= B		-20	2.76	-3					(16) (28)
								-11	7.3	-3					(18)
								0	2.66	-2					
								10	6.9	-2					
								20	2.29	-1	15.9	1.9	11		(16) (28)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.73		$CH_3I + Cl^-$	$(CH_3)_2CO$	$10^2A \simeq 6$; $10^2B = 3$	$LiClO_4$	0.11	k AB	-10	1.29	-4				*	(30)
								0	3.79	-4					
								14	1.80	-3					
								25	4.60	-3					
								34	9.64	-3	16.0	2.5	9		
.74	.2	$CH_3I + Br^-$	H_2O	A = 0.06; B = 0.1 L = 0.06; M = 0.15			k AB	20	2.69	-5				*	(38)
								35	1.35	-4					
								51	6.70	-4					
								67	2.41	-3	19.3	6	9		
			$(CH_2OH)_2$	$10^2L = 4$-5; $10^2M = 3$-10 4 3-5 4 10 4 3			k AB	15	6.0	-5				*	(37)
								25	2.13	-4					
								25	1.89	-4					
								35	6.90	-4					
								45	2.05	-3	21.4	1.1	12		
			$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2.3$	Li^+	= B	k AB	-11	1.16	-2				*	(19)
								0	3.94	-2					
								8	9.60	-2					
								16	2.19	-1	16.3	2.5	11		
.75	.3	$C_2H_5Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04			k AB	50	6.5	-5				*	(10)
								60	1.2	-4					
.76		$C_2H_5Br + Cl^-$	$(CH_3)_2CO$	A = 0.12; B = 0.07	Li^+	= B	k AB	25	9.88	-5				*	(29)
								35	2.43	-4					
								45	6.17	-4					
								55	1.50	-3					
								65	3.14	-3	17.6	8	8		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.77		$C_2H_5Br + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $10^2B = 7$	Li^+	= B	k AB	0	6.1	-5				*	(14)
				4 2				17	7.14	-4					(18)
				5 7				20	6.5	-4					(14)
				4 2				32	3.52	-3					(18)
				" "				40	7.94	-3					
				" "				50	2.07	-2	18.8	1.0	11		
			$(CH_3)_2CO$	$10^2A = 4$-30; $10^2B = 2$-4	Na^+	= B	k AB	0	1.4	-4				*	(28)
				4 2	Na^+ or K^+	= B		20	1.18	-3				(18)	(28)
				" "				30	3.28	-3					(18)
				" "				40	8.90	-3	19.0	1.6	11		
				4 3	Na^+	= B		64	6.9	-2					(14)
				" "	K^+	= B		64	4.8	-2					
.78		$C_2H_5I + Cl^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 3.2$	$LiClO_4$	0.11	k AB	14	1.40	-4				*	(30)
								25	4.30	-4					
								35	1.13	-3					
								46	2.75	-3					
								54	5.26	-3	17.0	1.3	9		
.79		$C_2H_5I + Br^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2.3$	Li	= B	k AB	16	6.15	-3				*	(19)
								25	1.49	-2					
								32	3.02	-2					
								40	5.98	-2	17.7	1.3	11		
.80	.7	n-$C_3H_7Cl + I^-$	$(CH_3)_2CO$	$A \sim 2$; $10^2B = 1.5$-2	K^+	= B	k AB	30	4.8	-6				*	(16)
				0.2 4	...			50	2.8	-5					(10)
				" "	...			60	4.6	-5	19				
				~ 2 1.5-2	K^+			60	1.08	-4	20.4	3	9		(16)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.81	.8	$(CH_3)_2CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$			k AB	60	9.4	-7				*	([10])
				~ 2 ~ 2	K^+			60	1.32	-6					([16])
				" "				80	1.24	-5	25	6	10		
.82		$n\text{-}C_3H_7Br + Cl^-$	$(CH_3)_2CO$	$A = 0.12$; $10^2B = 7$	Li^+	= B	k AB	25	6.45	-5				*	([29])
								35	1.64	-4					
								44	4.10	-4					
								55	1.06	-3					
								65	2.15	-3	17.5	4	8		
.83		$n\text{-}C_3H_7Br + I^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2$	Li^+	= B	k AB	25	1.37	-3				*	([18])
								35	4.09	-3					
								45	1.08	-2	19.0	1.3	11		
					Na^+	= B		25	1.45	-3					
								35	4.24	-3					
								45	1.16	-2	19.6	4	11		
					K^+	= B		25	1.49	-3					
								35	4.50	-3					
								45	1.12	-2	19.5	3	11		
.84		$(CH_3)_2CHBr + Cl^-$	$(CH_3)_2CO$	$A = 0.12$; $10^2B = 7$	Li^+	= B	k AB	35	5.22	-6				*	([29])
								45	1.42	-5					
								55	3.49	-5					
								65	7.96	-5					
								80	2.42	-4	18.8	8	7		
.85		$(CH_3)_2CHBr + I^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2$	Li^+	= B	k AB	40	6.70	-5				*	([18])
								50	1.87	-4					
								60	4.88	-4	20.5	1.4	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.85		$(CH_3)_2CHBr + I^-$ *(continued)*	$(CH_3)_2CO$	$10^2A \sim 200$; $10^2B \sim 2$	K^+	= B	k AB	30	2.58	-5				*	([16])
				4 2	Na^+ or K^+			40	6.8	-5					([18])
								50	1.92	-4					
								60	3.10	-4	20.5	1.5	10		
				~ 200 ~ 2	K^+			60	7.3	-4	22	2	11		([16])
.86		$n\text{-}C_3H_7I + Cl^-$	$(CH_3)_2CO$	$10^2A \simeq 6$; $10^2B = 3.2$	$LiClO_4$	0.11	k AB	14	7.83	-5				*	([30])
								25	2.46	-4					
								35	6.11	-4					
								46	1.64	-3					
								55	3.47	-3	17.0	6	8		
.87		$n\text{-}C_3H_7I + Br^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2.3$	Li^+	= B	k AB	-6	3.07	-4				*	([19])
								8	1.70	-3					
								26	1.18	-2					
								37	3.44	-2	17.5	6	10		
.88		$(CH_3)_2CHI + Cl^-$	$(CH_3)_2CO$	$10^2A \simeq 6$; $10^2B = 3.2$	$LiClO_4$	0.11	k AB	25	1.26	-5				*	([30])
								35	3.48	-5					
								46	9.69	-5					
								55	2.03	-4					
								64	4.23	-4	18.0	2	8		
.89		$(CH_3)_2CHI + Br^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2.3$	Li^+	= B	k AB	40	1.71	-3				*	([19])
								50	4.38	-3					
								60	1.03	-2					
								70	2.23	-2	18.5	1.6	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.90	.12	$n\text{-}C_4H_9Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 3	K^+	= B	k AB	20	8.45	-7				*	(13)
								30	3.42	-6					
								40	1.30	-5					
				0.04-0.07 1.8				50	2.12	-5					(15)
				0.2 4	Li^+, Na^+ or K^+	= B		50	2.6	-5				(10) (11) (12)	
								60	6.5	-5	22	2	9		
.91		$(CH_3)_2CHCH_2Cl + Br^-$	An 90*	L = M = 0.07	Li^+	= M	k AB	69	~1.2	-6				*	(45)
.92	.13	$CH_3CH_2(CH_3)CHCl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	60	1.4	-6				*	(10)
.93	.15	$(CH_3)_3CCl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	60	1.15	-6				*	(10)
.94		$n\text{-}C_4H_9Br + Cl^-$	An 90*	A = B = 0.07	Li^+	= B	k AB	40	2.15	-5				*	(45)
								55	9.70	-5					
								69	3.51	-4	20.0	2.0	9		
.95		$n\text{-}C_4H_9Br + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	15	4.87	-4					(48)
								25	1.30	-3					
				0.06 2				25	1.80	-3					(1)
				0.2 4				35	3.18	-3	16.6	2	9		(48)
.96		$(CH_3)_2CHCH_2Br + Cl^-$	$(CH_3)_2CO$	A = 0.12; 10^2B = 7	Li^+	= B	k AB	25	1.53	-5				*	(29)
								35	4.08	-5					
								44	1.04	-4					
								55	2.87	-4	18.1	2.5	8		
			An 90*	A = B = 0.07	Li^+	= B		40	1.22	-6				*	(45)
								55	6.31	-6					
								69	2.49	-5	21.7	1.8	9		

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.97		$(CH_3)_2CHCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2$	Li^+, Na^+ or K^+	= B	kAB	40	3.15	-4				*	([18])
								50	8.44	-4					
								60	2.16	-3	19.9	1.9	10		
.98		$(CH_3)_3CBr + F^-$	SO_2	$10^2A = 3$-8; $10^2B = 1.1$	$(CH_3)_4N^+$	= B	kAB	-15	5.92	-5				*	([8])
				2.1				-15	6.37	-5					
				4.0				-15	7.52	-5					
				6.0				-15	1.06	-4					
				7.4				-15	1.15	-4					
.99		$(CH_3)_3CBr + Cl^-$	$(CH_3)_2CO$	$A = 0.12$; $10^2B = 7$	Li^+	= B	kAB	44	2.7	-6				*	([29])
								55	7.6	-6					
								65	1.94	-5	21.0	8	8		
.100		$(CH_3)_3CBr + I^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2$	K^+	= B	kAB	35	3.6	-6					([18])
								45	1.06	-5					
								52	2.26	-5					
								61	5.63	-5	22.0	1.6	10		
.101		$(CH_3)_3CBr + ICl$	CCl_4	$A = 0.34$; $10^3B = 2$-10		$-dB/dt = kB^2$		25	2.18	-1				*	([32])
		$\longrightarrow (CH_3)_3CCl + IBr$		0.17		$-dB/dt = 1.43\ dM/dt$		25	1.82	-1					
		$\longrightarrow$ (mixed dihalides)		0.086				25	1.15	-1					
				0.043				25	7.85	-2					
				0.022				25	3.70	-2					
.102		$(CH_3)_2CHCH_2I + Cl^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 3.2$	$LiClO_4$	0.11	kAB	26	1.71	-5				*	([30])
								35	4.16	-5					
								45	1.04	-4					
								55	2.58	-4					
								64	5.67	-4	17.8	2	8		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.103		$(CH_3)_2CHCH_2I + Br^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2.3$	Li^+	= B	k AB	37	1.19	-3				*	(19)
								49	3.80	-3					
								60	9.62	-3					
								75	2.72	-2	18.8	2	10		
.104	.16	$n\text{-}C_5H_{11}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	3.5	-5				*	(10)
								60	8.1	-5	18.3			(10)	(11)
.105	.17	$(CH_3)_2CHCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	4.4	-5				*	(10)
.106	.18	$CH_3CH_2CH_2(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	3.1	-6				*	(10)
.107		$C_2H_5CH(CH_3)CH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 2$	K^+	= B	k AB	25	1.10	-4					(1)
.108		$(CH_3)_3CCH_2Br + Cl^-$	$(CH_3)_2CO$	$A = 0.12$; $10^2B = 7$	Li^+	= B	k AB	100	4.25	-6				*	(29)
								110	8.51	-6					
								120	1.74	-5					
								130	3.47	-5	21.7	2.5	7		
.109		$(CH_3)_3CCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $10^2B = 7$	Li^+, Na^+ or K^+	= B	k AB	64	2.8	-6				*	(14)
				4 2				65	4.4	-6					(18)
								73	1.02	-5					
								81	2.3	-5					
					Li^+	= B		90	5.31	-5					
								98	1.14	-4	24.0	1.6	10		
.110		$(CH_3)_3CCH_2I + Cl^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 3.2$	$LiClO_4$	0.11	k AB	80	1.88	-6				*	(30)
								100	1.02	-5					
								110	2.17	-5					
								120	4.57	-5	22.0	8	7		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.111		$(CH_3)_3CCH_2I + Br^-$	$(CH_3)_2CO$	$10^2L = 4$; $10^2M = 2.3$	Li^+	= B	k AB				23.1	1.3	10	*	(19)
.112	.19	$n\text{-}C_6H_{13}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50 60	3.34 8.15	-5 -5	19			* (9)	(10) (10)
.113	.20	$C_2H_5CH_2CH_2(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	5.25	-6				*(9)	(10)
.114		$C_2H_5CH_2(C_2H_5)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	2.81	-6				*	(9)
.115	.21	$C_2H_5CH_2(CH_3)_2CCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	1.84	-6				*	(10)
.116		$(CH_3)_3CCH_2CH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 2$	K^+	= B	k AB	25	7.3	-5				*	(1)
.117	.22	$n\text{-}C_7H_{15}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50 60	3.2 7.8	-5 -5	19			*	(10)
.118		$n\text{-}C_7H_{15}Br + I^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 2$	K^+	= B	k AB	25	2.14	-3					(1)
.119		$(CH_3)_3CCH_2CH_2CH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 2$	K^+	= B	k AB	25	1.80	-3					(1)
.120	.24	$n\text{-}C_8H_{17}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50 60	3.5 8.5	-5 -5	19			*	(10)
.121	.25	$CH_3(CH_2)_5(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	1.7	-6				*	(10)
.122	.26	$n\text{-}C_{12}H_{25}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50 60	3.0 6.4	-5 -5	17			*	(10)
.123	.27	$n\text{-}C_{14}H_{29}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50 60	2.5 6.2	-5 -5	19			*	(10)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.124	.28	$n\text{-}C_{16}H_{33}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	2.3	-5				*	(10)
								60	5.8	-5	19				
.125	.29	$n\text{-}C_{30}H_{61}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	2.3	-5				*	(10)
								60	5.8	-5	19				
		Cyclo alkyl halide													
.126		$\overline{CH_2CH_2CH}Br + I^-$	$(CH_3)_2CO$	$A = 0.18;\ 10^2B = 3.4$	K^+	= B		100	(no measurable reaction)						(43)
.127		$\overline{CH_2CH_2CH_2CH}Br + I^-$	$(CH_3)_2CO$	$A = 0.13;\ 10^2B = 4$			k AB	73	3.08	-5				*	(17)
								80	5.84	-5					
								92	1.86	-4					(17)(43)
								99	3.58	-4					(17)
								110	9.04	-4	24.5	9	10		
.128		$\overline{CH_2CH_2CH_2CH}I + Br^-$	$(CH_3)_2CO$	$L = 0.13;\ 10^2M = 4$			k AB	73	6.14	-4				*	(17)
								80	1.02	-3					
								92	2.62	-3					
								99	4.62	-3					
								110	9.51	-3	19.9	2.2	9		
.129		$\overline{CH_2(CH_2)_3CH}Cl + I^-$	$(CH_3)_2CO$		K^+	= B	k AB	58	1.95	-6				*	(6)
.130		$\overline{CH_2(CH_2)_3CH}Br + I^-$	$(CH_3)_2CO$	$A = 0.13;\ 10^2B = 4$			k AB	36	7.39	-5				*	(17)
								58	6.22	-4					(17)(43)
								69	1.69	-3					(17)
								78	3.73	-3	20.4	2.0	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.131		$\overline{CH_2(CH_2)_3}CHI + Br^-$	$(CH_3)_2CO$	L = 0.13; 10^2M = 4			k AB	36	1.06	-3				*	(17)
								58	7.35	-3					
								69	1.82	-2					
								78	3.76	-2	18.6	1.4	10		
.132		$\overline{CH_2(CH_2)_4}CHBr + Cl^-$	An 90*	A ≃ B ≃ 0.07	Li^+	= B	$-dA/dt = k$ AB; $k = k_S + k_E$								(45)
		$\longrightarrow C_6H_{11}Cl + Br^-$						69	3.69	-6					
		$\longrightarrow C_6H_{10} + HBr + Cl^-$						69	k_S = 1.3	-6					
.133		$\overline{CH_2(CH_2)_4}CHBr + I^-$	$(CH_3)_2CO$	A = 0.06; 10^2B = 2 .13 4	K^+ ...	= B	k AB	60	2.40	-5				*	(1)
								73	3.21	-5					(17)
								89	1.44	-4					(17) (43)
								99	3.22	-4					(17)
								110	8.08	-4	23.5	2.1	10		
.134		$\overline{CH_2(CH_2)_4}CHI + Br^-$	$(CH_3)_2CO$	L = 0.13; 10^2M = 4			k AB	73	6.98	-4				*	(17)
								89	2.86	-3					
								99	6.11	-3					
								110	1.45	-2	22.1	6	10		
.135		$\overline{CH_2(CH_2)_4}CHCH_2Br + Cl^-$	An 90*	A = B = 0.07	Li^+	= B	k AB	40	8.86	-7				*	(45)
								55	4.84	-6					
								69	1.97	-5	22.3	3	9		
.136		$\overline{CH_2(CH_2)_5}CHBr + I^-$	$(CH_3)_2CO$	A = 0.13; 10^2B = 4			k AB	37	4.73	-5				*	(17)
								48	1.43	-4					
								58	3.95	-4					
								73	1.53	-3	20.4	1.1	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.137		$\overline{CH_2(CH_2)_5CH}I + Br^-$	$(CH_3)_2CO$	L = 0.13; 10^2M = 4			k AB	37	7.23	-4				*	([17])
								48	1.93	-3					
								58	4.78	-3					
								73	1.62	-2	18.2	5	9		
.138		$\overline{CH_2(CH_2)_4CH}CH_2CH_2Cl + Br^-$	An 90*	L = M = 0.07	Li^+	= M	k AB	55	~7	-7				*	([45])
.139		$\overline{CH_2(CH_2)_4CH}CH_2CH_2Br + Cl^-$	An 90*	A = B = 0.07	Li^+	= B	k AB	40	1.30	-5				*	([45])
								55	6.17	-5					
								69	2.21	-4	20.3	2	9		
.140		$\overline{CH_2(CH_2)_6CH}Br + I^-$	$(CH_3)_2CO$	A = 0.13; 10^2B = 4		= B	k AB				21.2	1.0	10	*	([17])
.141		$\overline{CH_2(CH_2)_6CH}I + Br^-$	$(CH_3)_2CO$	L = 0.13; 10^2M = 4			k AB				19.5			*	([17])
.142		$C_{10}H_{17}Cl + I^-$ (bornyl chloride)	$(CH_3)_2CO$	A ≃ 2; 10^2B = 1-4	K^+	= B	k AB	80	<1	8					([16])
Hydroxy substituted alkyl halide															
.143		$HOCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	50	4.5	-5				*	([33])
								60	1.29	-4	22	6	10		
.144		$HOCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	35	1.02	-5				*	([33])
								45	3.18	-5	22	4	10		
Alkoxyl substituted alkyl halide															
.145	.4	$CH_3OCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	0	~1.2	-4				*	([12])
								10	~3.9	-4					

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.146		$CH_3OCH_2CH_2Br + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	15	5.47	-5				*	(48)
								25	1.67	-4	19	1	10		
.147		$C_2H_5OCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	35	9.8	-7				*	(48)
.148		$C_2H_5OCH_2CH_2Br + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	25	1.6	-4				*	(48)
.149		n-$C_4H_9OCH_2CH_2Br + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	15	4.80	-5				*	(48)
								25	1.46	-4					
								35	3.82	-4	18.2	3	9		
Keto-substituted alkyl halide															
.150	.10	$CH_3COCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	0	4.8	-3				*	(12)
								10	1.8	-2	20	5	13		
Carboxy-substituted alkyl halide															
.151	.9	$C_2H_5OOCCl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	25	6.0	-5				(10) (11) (12) *	
.152	.14	$C_2H_5OOCCH_2Cl + I^-$	$(CH_3)_2CO$	10^2A = 6; 10^2B = 1.5	K^+	= B	k AB	0	3.78	-4				*	(36)
								20	3.25	-3		1.9	10		
				20 4				25	4.05	-3				(10) (11) (12)	
								30	6.68	-3	17.1	1.4	10		
.153		$C_2H_5OOCCH_2Br + I^-$	$(CH_3)_2CO$	10^3A = 6; 10^3B = 5	K^+	= B	k AB	0	5.34	-1				*	(36)
								20	2.27	0	11.5	9	8		
.154	.6	$NH_2COCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	25	2.3	-4				*	(12)
								30	3.8	-4					
								50	2.53	-3	18.3	6	9		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.155		$C_2H_5OOCCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	4.26	-5				*	(11)
.156		$C_2H_5OOC(CH_3)CHBr + I^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^3B = 5$	K^+	= B	k AB	0	8.22	-4				*	(36)
								20	7.73	-3	17.8	1.5	11		
.157		$C_2H_5OOCCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	4.39	-5				*	(11)
.158		$C_2H_5OOCCH_2(CH_2)_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	3.60	-5				*	(11)
.159		l-$HOOCCH_2(COOH)CHCl + Br^-$	H_2O	$A = 0.18$; $B = 2$			k AB	50	7.25	-7				* (41)	(42)
								62	2.76	-6					
								75	9.83	-6					
								88	3.54	-5	23.5	6.2	9		
.160		l-$HOOCCH_2(COOH)CHBr + Cl^-$	H_2O	$A = 0.18$; $B = 2$			k AB	50	3.88	-6				* (41)	(42)
								62	1.45	-5					
								75	5.50	-5					
								88	1.88	-4	23.6	4.0	10		
.161	.23	$(C_2H_5OOC)_2CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	0	8.3	-3				*	(12)
								10	1.5	-2					
Carboxylate-substituted alkyl halide															
.162	.11	$CH_3COOCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	3.7	-4				*	(12)
								30	6.2	-4	18	1	10		
.163		$C_6H_5COOCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	25	1.1	-4				*	(33)
								35	2.08	-4	12				

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.164		$C_6H_5COOCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	50	1.19	-5				*	(33)
								60	3.09	-5	21				
.165		$C_6H_5COOCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	25	2.88	-6				*	(33)
								35	1.76	-5	33				
Nitrile substituted alkyl halide															
.166	.5	$CNCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	10	1.42	-3				*	(12)
								20	4.5	-3	19				
Silyl-substituted alkyl halide															
.167		$(CH_3)_3SiCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 3	K^+	= B	k AB	20	2.22	-5				*	(13)
								30	7.45	-5					
								40	2.26	-4	21.1	1.2	11		
				~0.04 ~2				50	3.33	-4				*	(15)
.168		$C_6H_5(CH_3)_2SiCH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A \simeq 4$; $10^2B \simeq 2$	K^+	= B	k AB	50	1.88	-4	20			*	(15)
.169		p-$CH_3C_6H_4(CH_3)_2SiCH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A \simeq 4$; $10^2B \simeq 2$	K^+	= B	k AB	50	1.47	-4	21			*	(15)
.170		p-$CH_3OC_6H_4(CH_3)_2SiCH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A \simeq 4$; $10^2B \simeq 2$	K^+	= B	k AB	50	1.45	-4	22			*	(15)
.171		p-$ClC_6H_4(CH_3)_2SiCH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A \simeq 4$; $10^2B \simeq 2$	K^+	= B	k AB	50	4.31	-4	21			*	(15)
.172		$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 3	K^+	= B	k AB	20	1.05	-5				*	(13)
								30	3.50	-5					
								40	1.07	-4	21.2	7	10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.173		$\overline{O[Si(CH_3)_2O]_3}Si(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 3$	K^+	= B	k AB	20	5.86	-6				*	(13)
								30	1.97	-5					
								40	6.20	-5	21.5	6	10		
Alkyl thio-substituted alkyl halide															
.174		$CH_3SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	4.02	-5				*	(34)
								60	1.07	-4	21	5	9		
.175		$CH_3SCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	6.68	-5				*	(34)
								60	1.52	-4	17				
Halogen-substituted alkyl halide															
.176		$ClCH_2Cl + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	50	4.22	-6				*	(28)
								60	1.68	-5	29	2	14		
.177		$ICH_2Cl + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	50	1.55	-6					(28)
.178		$FCH_2Br + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	20	6.4	-4					(28)
								50	1.35	-2	19	1.0	11		
.179		$ClCH_2Br + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	20	7.3	-5					(28)
								36	4.73	-4					
								50	2.18	-3	20.9	2.8	11		
.180		$BrCH_2Br + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	20	4.06	-5				*	(28)
								36	3.20	-4					
								50	1.38	-3	22	1.1	12		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.181		$ICH_2Br + I^-$	$(CH_3)_2CO$	$A \simeq 0.3$; $10^2B \simeq 4$	Na^+	= B	k AB	20	5	-5					(28)
								50	1.0	-3	18	1	9		
.182		$FCH_2CH_2Br + I^-$	CH_3OH	$10^2A = 9$; $10^2B = 5$	K^+	= B	k AB	40	5.5	-6					(27)
.183		$BrCH_2CH_2Br + I^- \longrightarrow$ (elimination see 422.477.1)													(27)
.184		$Cl_2CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A \simeq 2$; $10^2B = 1$-4	K^+	= B	k AB	60	1.44	-6				*	(16)
								80	1.00	-5	22	4	8		
.185		$CH_3CHClCH_2Cl + I^-$	$(CH_3)_2CO$	$A \simeq 2$; $10^2B = 1$-4	K^+	= B	k AB	60	9.9	-6				*	(16)
								80	5.42	-5	19	3	7		
		Unsaturated alkenyl halide													
.186		$CH_2{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 3.7$	K^+	= B	k AB	0	2.28	-5					(6)
				0.2 4				20	1.41	-4				*	(22) (47)
				0.1 2				25	3.18	-4	15	1	7		(44)
				0.02 2				25	2.8	-3					
.187		$CH_3CH{:}CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	< 1	-5				*	(23)
.188		$CH_2{:}CHCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 1.5$; $10^2B = 1$	K^+	= B	k AB	25	1.22	-1					(1)
.189		$CH_3CH{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	3.41	-4				*	(47)
.190		$CH_2{:}C(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	2.23	-4				*	(22) (47)
.191		$CH_2{:}CH(CH_3)CHCl + I^-$	$(CH_3)_2CO$		K^+	= B	k AB	20	1.4	-6				*	(40)
								50	3.1	-5	24	3	11		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.192		$(CH_3)_2C{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	4.6	-3				*	(21)
.193		*cis*-$CH_3CH{:}C(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	7.4	-4				*	(24) (47)
.194		*trans*-$CH_3CH{:}C(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	5.8	-3					(24)
Unsaturated alkynyl halide															
.195		$CH_3CH_2CH_2CH_2C{:}CCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 1.5$; $10^2B = 1$	K^+	= B	k AB	25	6.9	-2					(1)
.196		$(CH_3)_3CC{:}CCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 1.5$; $10^2B = 1$	K^+	= B	k AB	25	8.7	-2				*	(1)
Aryl-substituted alkyl halide															
.197	.30	$C_6H_5CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	0	3.35	-4				*	(9a)
				≃ 2 2-4				20	3.39	-4					(16)
				0.2 4				25	5.0	-4					(10) (11) (12)
				0.16 3-4				25	5.8	-4					(44)
				0.08 3				25	1.0	-3					
				0.02 0.4				25	1.2	-2					
				~ 2 2-4				30	9.5	-4					(16)
				0.2 4				30	8.4	-4					(10) (12)
				" "				50	5.0	-3	18.3	1.3	10		
.198		$C_6H_5CH_2Br + ICl \longrightarrow$ $C_6H_5CH_2Cl + IBr$	CCl_4	$10A = 1$-4; $10^3B = 2$-4			k AB^2	25	1.98	-2				*	(31)
				8				25	2.43	-2					
.199		$C_6H_5CH_2Br + I^-$	$(CH_3)_2CO$		K^+	= B	k AB	0	2.89	-2					(5)
				$A \simeq 2$; $10^2B \simeq 2$-4				20	2.32	-1	17	5	11		(16)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.200		$C_6H_5CH_2I + ICl \longrightarrow C_6H_5CH_2Cl + I_2$	CCl_4	$10^2A = 3-11$; $10^4B = 5-20$			$k\,AB^2$	25	1.08	0				*	(31)
.201		$o\text{-}CH_3C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 2	K^+	= B	$k\,AB$	0	3.68	-4					(9a)
				0.2 4				0	4.05	-4					
.202		$p\text{-}CH_3C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$	A ≃ 0.1; 10^2B = 2	K^+	= B	$k\,AB$	0	5.1	-5					(9a)
				0.2 4				0	5.46	-5					
				2 2-4				20	5.00	-4					(16)
								30	1.44	-3	18	1	10		
.203		$p\text{-}CH_3C_6H_4CH_2Br + I^-$	$(CH_3)_2CO$				$k\,AB$	0	4.23	-2					(5)
.204	.31	$C_6H_5CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	$k\,AB$	50	2.98	-5				*	(12)
								60	6.91	-5	18	4	7		
.205		$C_6H_5(CH_3)CHCl + I^-$	$(CH_3)_2CO$	10^2A = 5; B = 0.1	Na^+	= B	$k\,AB$	44	2.49	-5					(9a)
.206		$C_6H_5CH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	$k\,AB$	50	4.56	-5				*	(12)
								60	1.02	-4	17	3	7		
.207		$2,4\text{-}(CH_3)_2C_6H_3CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 2	K^+	= B	$k\,AB$	0	1.34	-3					(9a)
				0.2 4				0	1.52	-3					
.208		$2,6\text{-}(CH_3)_2C_6H_3CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 2	K^+	= B	$k\,AB$	0	6.00	-3					(9a)
.209		$o\text{-}CH_3C_6H_4(CH_3)CHCl + I^-$	$(CH_3)_2CO$	10^2A = 5; B = 0.1	Na^+	= B	$k\,AB$	44	8.04	-4					(9a)
.210		$p\text{-}CH_3C_6H_4(CH_3)CHCl + I^-$	$(CH_3)_2CO$	10^2A = 5; B = 0.1	Na^+	= B	$k\,AB$	44	6.07	-5					(9a)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.211		$C_6H_5(CH_2)_3CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	3.94	-5				*	(11)
								60	8.65	-5	17	1	7		
.212		$2,4,6\text{-}(CH_3)_3C_6H_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1$; $10^2B = 2$	K^+	= B	k AB	0	9.50	-3					(9a)
.213		$2,4\text{-}(CH_3)_2C_6H_3(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $B = 0.1$	Na^+	= B	k AB	44	2.49	-3					(9a)
.214		$2,6\text{-}(CH_3)_2C_6H_3(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $B = 0.1$	Na^+	= B	k AB	44	2.75	-4					(9a)
.215		$2,4,6\text{-}(CH_3)_3C_6H_2(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $B = 0.1$	Na^+	= B	k AB	44	1.73	-3					(9a)
.216		$p\text{-}(CH_3)_3CC_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$				k AB	0	3.92	-2					(5)
.217		$C_6H_5(CH_2)_4CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	8.25	-5				*	(11)
.218		$C_6H_5(CH_2)_5CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	8.51	-5				*	(11)
.219		$C_6H_5(CH_2)_5CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	60	8.12	-5				*	(11)
.220		$(C_6H_5)_2CHCl + F^-$	SO_2	$A = 0.12$; $10^2B = 1.5$	$(CH_3)_4N^+$	= B	k A	-17	8	-4					(2)
				10				-17	1.2	-3					
				3-10	$(C_2H_5)_4N^+$	= B		-17	1.2	-3					
.221		$(C_6H_5)_3CCl + F^-$	C_6H_6	$10^2A \simeq 3$; $10^2B = 2\text{-}6$	$(C_{18}H_{38})_2(CH_3)_2N^+$	= B	k A	0	9.5	-5				*	(46)
.222	.33	$(C_6H_5)_3CCl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	0	5.25	-3				*	(12)
.223		$p\text{-}NO_2C_6H_4CH_2Cl + Br^-$	AnM 5*	$10^2A = 5$; $10^3B = 3\text{-}300$	Li^+	= B	k AB	0	1.27	-3				*	(7)
								30	7.09	-2	21.5	2	14		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.224		p-$NO_2C_6H_4CH_2Cl + Li^+Br^-$	AnM 5*	$10^2A = 5$; $10^3B = 3$-300			k AB	0	1.92	-4				*	(7)
								30	1.06	-2	22	8	13		
.225		p-$NO_2C_6H_4CH_2Br + Cl^-$	AnM 5*	$10^2L \simeq 5$; $10^3M = 3$-300	Li^+	= M	k AB	0	1.8	-3				*	(7)
								30	4.8	-2	18	4	11		
.226	.51	o-$ClC_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	25	1.72	-3				*	(10)
								30	2.80	-3	18	3	10		
.227		m-$ClC_6H_4(C_6H_5)CHCl + F^-$	SO_2	$10^2A \simeq 7$; $10^3A = 2.8$	$(CH_3)_4N^+$	= B	k A	-11	2.38	-5				*	(2) (3)
				8.7				-11	2.82	-5					
				19				-11	4.00	-5					
				25				-11	4.80	-5					
				50				-11	7.70	-5					
				5.7	$(CH_3)_4N^+(Cl^-)$	0.046		-11	7.50	-5					
.228		m-$ClC_6H_4(C_6H_5)CHCl + I^-$	SO_2	$10^2A \simeq 7$; $10^3B = 2.8$	NH_4^+	= B	k A	-11	4.1	-5				*	(2) (3)
				6.8				-11	5.6	-5					
Aryl-substituted alkenyl halide															
.229		$CH_2{:}C(C_6H_5)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	20	3.16	-4				*	(25)
Arylalkoxy-substituted alkylhalide															
.230		$C_6H_5OCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	7.94	-6				*	(33)
								60	2.2	-5	21	2	9		
.231		$C_6H_5OCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	4.44	-5				*	(33)
								60	1.19	-4	21	7	9		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.232		$C_6H_5O(CH_2)_3CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	3.66	-5				*	(33)
								60	1.00	-4	21	1	10		
.233		α-$C_{10}H_7OCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	8.7	-6				*	(35)
								60	2.54	-5	23	2	10		
.234		β-$C_{10}H_7OCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	8.8	-6				*	(35)
								60	2.46	-5	22	6	9		
.235		α-$C_{10}H_7OCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	5.34	-5				*	(35)
								60	1.31	-4	19	5	8		
.236		β-$C_{10}H_7OCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	50	5.36	-5				*	(35)
								60	1.36	-4	19	5	8		
Aryl-oxo-substituted alkylhalide															
.237	.34	$C_6H_5COCl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	0	1.0	-4				*	(11) (12)
.238	.35	$C_6H_5COCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	-10	3.78	-3					(10) (11) (12)
								0	1.43	-2	19	2	13	*	
.239		$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	40	7.61	-4				*	(11)
								50	2.30	-3	22	2	11		
.240	.36	$C_6H_5COCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2;\ 10^2B = 4$	K^+	= B	k AB	25	5.41	-4				*	(11) (12)
Aryl-carboxy-substituted alkyl halide															
.241		l-$HOOC(C_6H_5)CHCl + Br^- \longrightarrow$ d-$HOOC(C_6H_5)CHBr + Cl^-$	H_2O	$10^2A = 1.5;\ B = 1.0$	H^+	= B	k AB	25	4.09	-6				*	(49)
								35	1.18	-5					
								49	5.19	-5	20.0	1.9	9		

Supplement 1956

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.242		l-HOOC(C_6H_5)CHBr + Cl^- ⟶ d-HOOC(C_6H_5)CHCl + Br^-	H_2O	$10^2A = 1.5$; $B = 1.0$	H^+	= B	k AB	25	2.09	-5				*	(49)
								35	6.02	-5					
								49	2.64	-4	19.8	7	9		
Aryl-thio-substituted alkyl halide															
.243		$C_6H_5SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	1.50	-5				*	(35)
								55	2.53	-5					(4)
								60	4.08	-5	21	5	9		(35)
.244		$C_6H_5SCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	50	7.3	-5				*	(35)
								55	9.16	-5					(4)
								60	1.79	-4	19	6	8		(35)
.245		o-$NO_2C_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	55	5.00	-5					(4)
.246		m-$NO_2C_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	55	5.25	-5					(4)
.247		p-$NO_2C_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	55	7.15	-5					(4)
.248		p-$NO_2C_6H_4SCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	55	2.32	-4					(4)
.249		p-$NO_2C_6H_4CH_2SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2$; $10^2B = 4$	K^+	= B	k AB	55	5.98	-5					(4)
Aryl sulfonyl-substituted alkyl(alkenyl)halide															
.250		p-$CH_3C_6H_4SO_2CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A = 2.5$; $10^2B = 3$	K^+	= B	k AB	0	< 1	-8				*	(6)
.251		$C_6H_5SO_2CH{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1$; $10^2B = 3.1$	K^+	= B	k AB	0	3.6	-4				*	(6)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.252		p-$CH_3C_6H_4SO_2CH{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 3.1	K^+	= B	k AB	0	3.06	-4					(6)
Nitrile substituted alkenyl halide															
.253		$N{:}CCH{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 3.6	K^+	= B	k AB	0	3.92	-4					(6)
Halogen-substituted alkenyl halide															
.254		$CH_2{:}CHCHCl_2 + I^- \longrightarrow$ $CH_2{:}CHCHClI + Cl^-$	$(CH_3)_2CO$		K^+	= B	k AB	25 50	8 2.0	-7 -5	25	8	11		(40)
.255		$CH_2{:}CClCH_2Cl + I^-$	$(CH_3)_2CO$		K^+	= B	k AB	20	1.01	-4				*	(22)
.256		*cis*-$CHCl{:}CHCH_2Cl + I^-$ (low boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	1.20	-3				*	(22)
.257		*trans*-$CHCl{:}CHCH_2Cl + I^-$ (high boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	4.04	-4				*	(22)
.258		$CH_2{:}CBrCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	1.22	-4				*	(22)
.259		*cis*-$CHBr{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	2.8	-3				*	(23)
.260		*trans*-$CHBr{:}CHCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	1.6	-4				*	(23)
.261		α-$CH_3CCl{:}CHCH_2Cl + I^-$ (low boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	2.9	-3				*(20) (26)	

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.262		β-$CH_3CCl{:}CHCH_2Cl + I^-$ (high boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	8.60	-3				*	(20) (26)
.263		$CHCl{:}C(CH_3)CH_2Cl + I^-$ (low boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	4.6	-3				*	(22)
.264		$CHCl{:}C(CH_3)CH_2Cl + I^-$ (high boiling isomer)	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	1.17	-3				*	(22)
.265		$Cl_2C{:}C(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; 10^2B = 4	K^+	= B	k AB	20	5	-3				*	(22)
		Carboxy and halogen substituted alky halide													
.266		$C_2H_5OOCCHFCl + I^- \longrightarrow C_2H_5OOCCHFI + Cl^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 1.5	K^+	= B	k AB	20 40	3.1 6.3	-6 -5	27.5	1.0	15	*	(36)
.267		$C_2H_5OOCCHCl_2 + I^- \longrightarrow C_2H_5OOCCHClI + Cl^-$	$(CH_3)_2CO$	A = 0.1; 10^2B = 1.5	K^+	= B	k AB	20 40	1.89 2.2	-5 -4	22.3	8	11	*	(36)
.268		$C_2H_5OOCCHFBr + I^- \quad C_2H_5OOCCHFI + Br^-$	$(CH_3)_2CO$	10^2A = 6; 10^3B = 5	K^+	= B	k AB	0 20	1.66 8.48	-3 -3	12.9	4	7	*	(36)
.269		$C_2H_5OOCCHClBr + I^- \longrightarrow C_2H_5OOCCHClI + Br^-$	$(CH_3)_2CO$	10^2A = 6; 10^3B = 5	K^+	= B	k AB	0 20	2.14 2.22	-4 -3	18.6	1.7	11	*	(36)
.270		$C_2H_5OOCCHBr_2 + I^- \longrightarrow C_2H_5OOCCHBrI^- + Br^-$	$(CH_3)_2CO$	10^2A = 6; 10^2B = 1.5	K^+	= B	k AB	0 20	9.22 1.12	-5 -3	19.8	7	11	*	(36)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.271		$C_2H_5OOCCFBr_2 + I^- \longrightarrow C_2H_5OOCCFBrI^- + Br^-$	$(CH_3)_2CO$	$10^2A = 6$; $10^2B = 1.5$	K^+	= B	k AB	20 40	6.40 5.90	-5 -4	20.1	6	10	*	(36)
Benzimidazolyl-substituted alkyl halide															
.272	.38	$\overline{NHC_6H_4N{:}C}CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	$10^2A = 5$; $10^2B = 2$ 2 2 1 2 2.5 1	K^+	= B	k AB	25 25 25 25	1.22 2.54 3.82 4.55	-2 -2 -2 -2				*	(44)
.273	.41	$\overline{N(CH_3)C_6H_4N{:}C}CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2A = 2$; $10^2B = 2$ 2.5 1 1 2	K^+	= B	k AB	25 25 25	6.95 2.54 7.11	-2 -1 -1				*	(44)
.274	.42	$\overline{N(CH_3)C_6H_4N{:}C}CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	$10^2A = 4$; $10^2B = 2$ 3 2 2.5 1 0.5 2	K^+	= B	k AB	25 25 25 25	1.20 1.65 1.50 2.30	-2 -2 -1 -1				*	(44)
.275	.39	$\overline{NHC_6H_4N{:}C}CH(C_2H_5)Cl + I^-$	$(CH_3)_2CO$	$10^2A = 3$; $10^2B = 2$ 1.6 2 2.5 1 1 2	K^+	= B	k AB	25 25 25 25	1.26 4.9 5.7 9.3	-2 -2 -2 -2				*	(44)
.276	.40	$\overline{NHC_6H_4N{:}C}C(CH_3)_2Cl + I^-$	$(CH_3)_2CO$	$10^2A = 2$; $10^2B = 2$ 2.5 1 1 2	K^+	= B	k AB	25 25 25	6.5 2.42 4.26	-2 -1 -1				*	(44)

SOLVENTS

An90*	$(CH_3)_2CO$ 90 vol % + H_2O	(45)
AnM5*	$(CH_3)_2CO$ + 5 vol % CH_3OH + 0.31M in H_2O	(7)

COMMENTS

Classification.

(.71) - (.125)	Saturated alkyl halides
(.126) - (.142)	Saturated cyclo-alkyl halide
(.143) - (.144)	Hydroxy-substituted alkyl halide
(.145) - (.149)	Alkoxyl-substituted alkyl halide
(.150)	Keto-substituted alkyl halide
(.151) - (.161)	Carboxy-substituted alkyl halide
(.162) - (.165)	Carboxylate-substituted alkyl halide
(.166)	Nitrile-substituted alkyl halide
(.167) - (.173)	Silyl-substituted alkyl halide
(.174) - (.175)	Alkylthio-substituted alkyl halide
(.176) - (.185)	Halogen-substituted alkyl halide
(.186) - (.194)	Unsaturated alkenyl halide
(.195) - (.196)	Unsaturated alkynyl halide
(.197) - (.228)	Aryl-substituted alkyl halide
(.229)	Aryl-substituted alkenyl halide
(.230) - (.236)	Arylalkoxy-substituted alkyl halide
(.237) - (.240)	Aryloxo-substituted alkyl halide
(.241) - (.242)	Aryl-carboxy substituted alkyl halide
(.243) - (.249)	Arylthio-substituted alkyl halide
(.250) - (.252)	Arylsulfonyl-substituted alkyl halide
(.253)	Nitrile-substituted alkenyl halide
(.254) - (.265)	Halogen-substituted alkenyl halide
(.266) - (.271)	Carboxy and halogen-substituted alkyl halide
(.272) - (.276)	Benzimidazolyl-substituted alkyl halide

COMMENTS *(continued)*

General. Halogen exchange reactions usually studied in acetone as solvent using lithium, sodium or potassium salts. When sodium or potassium iodide used insoluble chloride or bromide separates and reaction goes to completion. When lithium salts are used reactions proceed to equilibrium and reverse reactions may be studied. Salt effects are observed and vary slightly with different halides.

Comments by Literature References. (9) (10) (11) (12) Units of rate constants converted to seconds and base e logarithms from original hours and base 10. (13) (15) Units converted to seconds from original hours. (20) (21) (22) Units converted to seconds and base e logarithms from original hours and base 10. (23) (24) (25) (26) Units converted to seconds from original hours. (31) (32) Units converted to seconds from original minutes. (33) (34) (35) Units converted to seconds and base e logarithms from original hours and base 10. (36) (40) Units converted to seconds from original hours. (41) (42) (43) Units converted to seconds from original minutes. (44) Units converted to seconds from original hours. (47) (48) Units converted to seconds and base e logarithms from original hours and base 10. (49) Units converted to seconds from original minutes.

Comments by Reaction. **(.71)** Rate law followed up to 70% reaction with reverse reaction considered negligible. Negative salt effect. **(.72)** Rate of forward reaction only. For simultaneous reverse reaction see (.74). **(.73)** Addition of $LiClO_4$ eliminates drift in rate constants with course of reaction. Reverse reaction considered negligible. **(.74)** In H_2O reaction is in competition with hydrolysis and reverse reaction. In ethylene glycol solvolysis is unimportant below 50°C. Rate constants are for forward reaction only. For competing reverse reaction see (.72). In $(CH_3)_2CO$ rate constants drift with progress of reaction. This is attributed to greater retarding salt effect of LiI than of the LiBr initially present. **(.75)** Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. **(.76)** Rate law followed up to 70% reaction with reverse reaction considered negligible. Negative salt effect. **(.77)** Rate constant for forward reaction only. For competing reverse reaction see (.79). Only about 10% conversion at equilibrium. Negative salt effect. **(.78)** In absence of added $LiClO_4$ rate constants drift with course of reaction. Reverse reaction considered negligible, see (.75). **(.79)** Rate constant for forward reaction only. For competing reverse reaction

COMMENTS *(continued)*

see (.77). Rate constants drift with course of reaction as LiI replaces LiBr. Values are calculated for rate near end of reaction as system approaches equilibrium. **(.80)** Rate constant for forward reaction only. For competing reverse reaction see (.86). Corrected to base e logarithm from uncorrected values in 1951 edition of Tables. **(.81)** Rate constant for forward reaction only. For competing reverse reaction see (.88). Corrected to base e logarithm from uncorrected values in 1951 edition of Tables. **(.82)** Reaction followed to 70% completion and reverse reaction considered negligible. **(.83)** Selected data. Rate constant for forward reaction only. For competing reverse reaction see (.87). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. **(.84)** Reaction followed to 70% completion and reverse reaction considered negligible. Negative salt effect. **(.85)** Rate constant for forward reaction only. For competing reverse reaction see (.89). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. **(.86)** Calculated rate constants drift with course of reaction in absence of added $LiClO_4$. For competing reverse reaction see (.80). **(.87)** Rate constant for forward reaction only. For competing reverse reaction see (.83). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Value used is that calculated for end of reaction as equilibrium is approached. **(.88)** Calculated rate constants drift with course of reaction in absence of added $LiClO_4$. Reverse reaction negligible, see (.81). **(.89)** Rate constant for forward reaction only. For competing reverse reaction see (.85). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Value used is that calculated for end of reaction as equilibrium is approached. **(.90)** Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. **(.91)** Approximate value giving order of magnitude only. Determined by getting best fit of data for reverse reaction. See (.96). **(.92) (.93)** Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. **(.94)** Rate constant for forward reaction only, but rate constant for reverse reaction not determined with precision. **(.96)** Reaction followed up to 70% completion in $(CH_3)_2CO$, and reverse reaction, (.91), considered negligible by ([29]). Negative

COMMENTS *(continued)*

salt effect. In $(CH_3)_2CO$ and H_2O mixture rate constant for forward reaction only. For competing reverse reaction see (.91). **(.97)** Selected data. Rate constant for forward reaction only. For competing reverse reaction see (.103). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Values calculated are for initial conditions. **(.98)** Rate constant for forward reaction only and values are for initial rates. Increase of calculated rate constants with increase in initial concentration of B attributed to a salt effect and at ionic μ:

$$\log k_\mu = \log k_o + 9.12 \times 10^{15}\, \mu\sigma / D^2T^2$$

where $\sigma = 0.93$ Å. Rate determining step involves formation of $(CH_3)_3C^+$ and ratio of competition of F^- to Br^- in reacting with $(CH_3)_3C^+$ determined to be 0.30. **(.99)** Reaction followed to only 40% completion as total halide increased with reaction indicating competing elimination reaction. Rate constants determined by graphical extrapolation to time zero. Negative salt effect. **(.101)** Reaction followed to only 25% completion as I_2 formed in later stages. Some isobutylene dihalide also formed. **(.102)** Calculated rate constants drift with progress of reaction in absence of added $LiClO_4$. Reverse reaction considered negligible. **(.103)** Rate constant for forward reaction only. For competing reverse reaction see (.97). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Value used is that calculated for end of reaction as system approaches equilibrium. **(.104)** Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. Calculated rate constants decrease with course of reaction. **(.105) (.106)** Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. **(.108)** Reaction followed to 70% completion and reverse reaction considered negligible. Negative salt effect. **(.109)** Rate constant for forward reaction only. For competing reverse reaction see (.111). Negative salt effect with LiI retarding reaction more than LiBr. **(.110)** Calculated rate constants drift with progress of reaction in absence of added $LiClO_4$. Reverse reaction considered to be negligible. **(.111)** Rate constant for forward reaction only. For competing reverse reaction see (.109). Calculated rate constants decrease with progress of reaction. This is attributed to greater negative salt effect of LiI than of LiBr. Value used is that calculated at end of reaction as system approaches equilibrium. **(.112) (.113) (.115) (.117) (.120) (.121) (.122)**

COMMENTS *(continued)*

(.123) (.124) (.125) Converted to base e logarithms from uncorrected values in 1951 edition of Tables. **(.127)** Rate constant for forward reaction only. For competing reverse reaction see (.128). **(.128)** Rate constant for forward reaction only. For competing reverse reaction see (.127). **(.129)** Reaction followed only to 27% completion as faint iodine coloration appears at this point. Calculated rate constants decrease about 4% in this range. **(.130)** Rate constant for forward reaction only. For competing reverse reaction see (.131). **(.131)** Rate constant for forward reaction only. For competing reverse reaction see (.130). **(.133)** Rate constant for forward reaction only. For competing reverse reaction see (.134). Some parallel elimination reaction noted by ([1]). **(.134)** Rate constant for forward reaction only. For competing reverse reaction see (.133). **(.135)** Rate constant for forward reaction only. Corrected for reverse reaction but rate constant for reverse reaction not given. **(.136)** Rate constant for forward reaction only. For competing reverse reaction see (.137). **(.137)** Rate constant for forward reaction only. For competing reverse reaction see (.136). **(.138)** Rate constant gives order of magnitude only. Determined by obtaining best fit for data of reverse reaction (.139). **(.139)** Rate constant for forward reaction only. For competing reverse reaction see (.138). **(.140) (.141)** Forward and reverse reactions. Actual rate constants not given only activation energies and frequency term for (.140). **(.145) (.150)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.151) (.152)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. Calculated rate constants decrease with progress of reaction. **(.154)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.155)** Calculated rate constants decrease with course of reaction. **(.156)** Reaction followed to only 35% completion due to subsequent decomposition of iodoester. **(.157) (.158)** Calculated rate constants decrease with course of reaction. **(.159)** Rate constant for forward reaction only. Accompanied by parallel elimination and racemization reactions see 422.471 and 112.470. For reverse reaction see (.160). **(.160)** Rate constant for forward reaction only. Accompanied by parallel elimination and racemization reactions see 422.471 and 112.470. For reverse reaction see (.159). **(.161) (.162) (.166)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.169)** Slight negative salt effect. **(.176) (.180)** Actual rate of ex-

COMMENTS *(continued)*

change is tabulated rather than half rate, (per halogen), listed by ([28]). **(.184) (.185)** Some iodine is also liberated during reaction. **(.187)** No measurable reaction after six hours. **(.192)** Rate constants decrease with progress of reaction. Value is average for first 40% reaction rather than average of all values by ([21]). **(.196)** Rate constants calculated graphically but decrease with course observed as first and last points fell below authors straight line. **(.197)** Converted to base e logarithms from uncorrected values in 1951 edition of Tables. Addition of H_2O observed by ([44]) to cause decrease in reaction rate. Values from 0.09 to 21% by weight of water are given. **(.198) (.200)** Third order rate constant calculated by dividing pseudo second order constant by concentration of A. Reaction performed in the dark to avoid halogenation. At concentrations of A and B > 1 M/l reaction much faster and some halogenation of benzene ring occurs. **(.211) (.219)** Calculated rate constants decrease with course of reaction. **(.221)** First order rate law valid for first 40% reaction only. Beyond this rate drops to less than 1% of initial rate when 50% of whichever reactant was in lower concentration is consumed. This is not an equilibrium effect. **(.222)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.223) (.224)** Rate constants for the forward reaction only. For competing reverse reaction see (.225). Authors consider total reaction to be best expressed as the sum of the parallel reactions (.223) and (.224) involving Br^- and the ion pair Br^-Li^+ respectively. **(.225)** Rate constant for forward reaction only. For competing reverse reaction see (.223) (.224). **(.226)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.227) (.228)** Calculated rate constants decrease with course of reaction. Value tabulated is that extrapolated to zero time. **(.237) (.238)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. Calculated rate constants decrease with course of reaction. **(.240)** Converted to base e logarithms from uncorrected value in 1951 edition of Tables. **(.241) (.242)** Rate constants of these opposing reactions calculated from analysis of polarimetric data involving simultaneous, exchange racemization and solvolysis reactions. See 112.470 and 212.471. **(.250)** No measurable reaction in 10 weeks. **(.251)** Calculated rate constants increase 15% in first 45% reaction. **(.255) (.256) (.257) (.258)** Only allyl halogen assumed to react, as $CH_3CH{:}CHCl$ gives no measurable exchange in 8 hr. See

COMMENTS *(continued)*

(.187). **(.259)** Reaction studied in mixture containing 95% cis- and 5% trans-isomer. Rate constant extrapolated to 100% cis-isomer. **(.260)** Reaction studied in mixture containing 75% trans-isomer and 25% cis-isomer. Rate constant extrapolated to 100% trans-isomer. **(.261) (.262)** Only allyl halogen assumed to react, as $CH_3CH{:}CHCl$ gives no measurable exchange in 8 hours. See (.187). **(.263) (.264) (.265)** Calculated rate constants decrease with course of reaction. Only allyl halogen assumed to react. See (.187). **(.266)** Reaction followed to only about 20% due to subsequent decomposition of iodoester. Negative test for F^-. **(.267)** Reaction followed to only 35% due to subsequent decomposition of iodoester. **(.268)** Reaction followed to 60%. Subsequent decomposition of iodoester occurs. Negative test for F^-. **(.269) (.270)** Reaction followed to only 35% due to subsequent decomposition of iodoester. **(.271)** Reaction followed to only 35% due to subsequent decomposition of iodoester. Negative test for F^-. **(.272)** Formula corrected from incorrect structure given in 1951 edition of Tables. **(.273)** Rate constants corrected by power of ten from values listed in 1951 edition of Tables. **(.274) (.275) (.276)** Formula corrected from incorrect structure given in 1951 edition of Tables.

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EXCHANGE
ON Vth GROUP ELEMENT
Halogen Replaced by Nitrogen on P

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $\underset{(A)}{(RO)_2OPX} + \underset{(B)}{2R_1R_2NH} \longrightarrow \underset{(L)}{(RO)_2OPNR_1R_2} + \underset{(M)}{R_1R_2NH_2^+} + X^-$

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$(CH_3O)_2OPCl + 2(n\text{-}C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAB$	-13	1.9	-2					
							0	3.9	-2	8	1	5		
.2	$(C_2H_5O)_2OPCl + 2(n\text{-}C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAB$	-13	8	-3					
							0	1.9	-2	8	5	4		
.3	$[(CH_3)_2CHO]_2OPCl + 2n\text{-}C_4H_9NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	25	3.0	-2					
.4	$[(CH_3)_2CHO]_2OPCl + 2(CH_3)_2CHCH_2NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	25	6.6	-2					
.5	$[(CH_3)_2CHO]_2OPCl + 2C_2H_5(CH_3)CHNH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	1.20	-2					
.6	$[(CH_3)_2CHO]_2OPCl + 2(CH_3)_3CNH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	2	-4					
.7	$[(CH_3)_2CHO]_2OPCl + 2C_6H_5NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	2	-6					
.8	$[(CH_3)_2CHO]_2OPCl + 2(C_2H_5)_2NH \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	1.1	-3					
.9	$[(CH_3)_2CHO]_2OPCl + 2(n\text{-}C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAB$	-13	7	-4					
							0	1.2	-3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.9	$[(CH_3)_2CHO]_2OPCl + 2(n\text{-}C_4H_9)_2NH \longrightarrow$ *(cont.)*	C_2H_5OH	$10^2A = 5$; $B = 0.1$			$-dA/dt = kAB$	25	5.5	-3					
							40	1.03	-2					
			2 0.05	$NaClO_4$	0.2		25	2	-2					
			2 0.1	NH_4NO_3	0.2		25	7	-2					
			4 0.1	L	0.04		25	8	-3					
			4 0.1	M	0.12		25	1.5	-2					
		C_6H_6	$10^2A=1.6$; $10^2B=8.3$			$-dA/dt = kAB$	25	6	-4					
			0.9 4.4	$(C_2H_5)_3N$	0.18		25	5	-4					
					0		40	1.1	-3					
					0		64	2.0	-3	8.9	2	4		
		$n\text{-}C_7H_{16}$					25	1.7	-4					
		Dioxane					25	8	-3					
		$(CH_3)_2CO$					0	8	-3					
							25	2.5	-2					
		CH_3NO_2					25	4	-2					
		$C_6H_5NO_2$					25	6	-2					
		CH_3CN					25	7.5	-2					
.10	$[(CH_3)_2CHO]_2OPCl + 2[C_2H_5(CH_3)CH]_2NH \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	1	-5					
							64	3	-5					
.11	$[(CH_3)_2CHO]_2OPCl + (C_2H_5)_3N \longrightarrow$ (products not determined but only one mole of amine consumed.)	C_6H_6				kAB	0	5	-5					

LITERATURE

I. Dostrovsky, M. Halmann, *CSL* **1953**, 511.

EXCHANGE
on Vth Group Element
Exchange of halogen for halogen on P

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments
.1	$(CH_3O)_2OPCl + F^- \longrightarrow (CH_3O)_2OPF + Cl^-$	C_2H_5OH		K^+	=B	kAB	0	(too fast to measure)					
.2	$(C_2H_5O)_2OPCl + F^- \longrightarrow (C_2H_5O)_2OPF + Cl^-$	C_2H_5OH		K^+	=B	kAB	0	2.8	-1				*
.3	$[(CH_3)_2CHO]_2OPCl + F^- \longrightarrow [(CH_3)_2CHO]_2OPF + Cl^-$	C_2H_5OH	10^3A = 5-14; 10^3B = 3-23	K^+	=B	kAB	0	3.0	-2				*
							25	2.3	-1	13	6	8	
		60% $C_2H_5OH + H_2O$		K^+	=B		25	3.9	-2				

COMMENTS

Reaction: **(.2)** Value of rate constant approximate as reaction almost too fast to measure. **(.3)** Value of rate constant in 60% C_2H_5OH solution corrected for parallel solvolysis reaction see 252.570.

LITERATURE

I. Dostrovsky, M. Halmann, *CSL* **1953**, 508.

ELIMINATION

Hydrogen ion elimination from CH bond activated by adjacent CO, (COOR), (CN), NO_2

Reaction types:

$$-\overset{|}{\underset{|}{C}}-H + B \longrightarrow -\overset{|}{\underset{|}{C}}^{-} + BH^{+}$$

$$-\overset{|}{\underset{|}{C}}-H + B'^{-} \longrightarrow -\overset{|}{\underset{|}{C}}^{-} + BH$$

Liquid phase

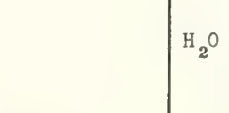
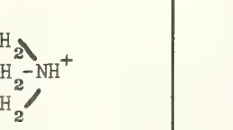
Amounts are in M/l. Rate constants are in M/l and sec.

* Coded solvents at end of Table.

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
		Single activating group NO_2													
.24	.11	$C_2H_5NO_2 + H_2O \longrightarrow CH_3CH{:}NO_2^- + H_3O^+$	B	A = 0.2-0.3	Br_2 or I_2	0-0.02	k A	15	9.0	-9				*	(8)
								26	4.05	-8					
								35	1.25	-7					
								70	4.4	-6	22.9	1.2	9		(5)
			"	~0.001	buffers	pH = 6.1		25	3.22	-8				*	(6)
					glycine + NaOH + NaCl	7.0		25	4.27	-8					
						8.0		25	8.33	-8					
						8.9		25	1.02	-7					
						10.0		25	3.14	-7					
						10.9		25	8.80	-7					
.25	.12	$C_2H_5NO_2 + OH^- \longrightarrow CH_3CH{:}NO_2^- + H_2O$	H_2O	A = B = 0.02-0.06			k AB	25	5.8	0	14.2	1.5	11	*	(1) (10)
					NaCl	0.011		25	5.75	0					
						0.02-0.05		25	5.55	0					
						0.06		25	5.75	0					
						0.09		25	5.85	0					
					$CaCl_2$	0.02		25	4.85	0					
						0.04		25	4.5	0					
						0.06		25	4.1	0					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.26	$C_2H_5NO_2 + C_2H_5NH_2 \longrightarrow$ $CH_3CH{:}NO_2^- + C_2H_5NH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.42	-2				*	([12])
.27	$C_2H_5NO_2 + n\text{-}C_3H_7NH_2 \longrightarrow$ $CH_3CH{:}NO_2^- + n\text{-}C_3H_7NH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.48	-2				*	([12])
.28	$C_2H_5NO_2 + (CH_3)_2CHNH_2 \longrightarrow$ $CH_3CH{:}NO_2^- + (CH_3)_2CHNH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.90	-2				*	([12])
.29	$C_2H_5NO_2 + n\text{-}C_4H_9NH_2 \longrightarrow$ $CH_3CH{:}NO_2^- + n\text{-}C_4H_9NH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.88	-2				*	([12])
.30	$C_2H_5NO_2 + (CH_3)_3CNH_2 \longrightarrow$ $CH_3CH{:}NO_2^- + (CH_3)_3CNH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.88	-2				*	([12])
.31	$C_2H_5NO_2 + n\text{-}C_6H_{13}NH \longrightarrow$ $CH_3CH{:}NO_2^- + n\text{-}C_6H_{13}NH_3^+$	H_2O	A = B = 0.01-0.03			k AB	0	1.88	-2				*	([12])
.32	$C_2H_5NO_2 + (C_2H_5)_2NH \longrightarrow$ $CH_3CH{:}NO_2^- + (C_2H_5)_2NH_2^+$	H_2O	A = B = 0.01-0.03			k AB	0	4.64	-2				*	([12])
.33	$C_2H_5NO_2 + [(CH_3)_2CH]_2NH \longrightarrow$ $CH_3CH{:}NO_2^- + [(CH_3)_2CH]_2NH_2^+$	H_2O	A = B = 0.01-0.03			k AB	0	4.34	-2				*	([12])
.34	$C_2H_5NO_2 + \overline{CH_2(CH_2)_4NH} \longrightarrow$ $CH_3CH{:}NO_2^- + \overline{CH_2(CH_2)_4NH_2}^+$	H_2O	A = B = 0.01-0.03			k AB	0	8.30	-2				*	([12])

Supplement 1958

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.35	$C_2H_5NO_2 + (C_2H_5)_3N \longrightarrow$ $CH_3CH{:}NO_2^- + (C_2H_5)_3NH^+$	H_2O	A = B = 0.01-0.03			k AB	0	5.20	-2				*	(12)
.36	$C_2H_5NO_2 +$  $\longrightarrow$ (quinuclidine) $CH_3CH{:}NO_2^- +$ 	H_2O	A = B = 0.01-0.03			k AB	0	9.8	-2				*	(12)
.37	$C_2H_5NO_2 + C_5H_5N \longrightarrow$ $CH_3CH{:}NO_2^- + C_5H_5NH^+$	H_2O	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	17	6.07	-5				*	(8) (11)
							25	1.49	-4					
							35	3.57	-4	16.6	2	8		
		Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	0	8.61	-6					
							25	1.08	-4					
							35	2.32	-4	15.8	4	7		
		Et 70*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	0	4.6	-7					
							25	5.87	-6					
							35	1.62	-5	17.1	2	7		
.38	$C_2H_5NO_2 + 2\text{-}CH_3C_5H_4N \longrightarrow$ $CH_3CH{:}NO_2^- + 2\text{-}CH_3C_5H_4NH^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	4.1	-4				*	(11)
.39	$C_2H_5NO_2 + 3\text{-}CH_3C_5H_4N \longrightarrow$ $CH_3CH{:}NO_2^- + 3\text{-}CH_3C_5H_4NH^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	2.20	-4				*	(11)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.40	$C_2H_5NO_2 + 4\text{-}CH_3C_5H_4N \longrightarrow$ $CH_3CH{:}NO_2^- + 4\text{-}CH_3C_5H_4NH^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	3.03	-4				*	(11)
.41	$C_2H_5NO_2 + 2,6\text{-}(CH_3)_2C_5H_4N \longrightarrow$ $CH_3CH{:}NO_2^- + 2,6\text{-}(CH_3)_2C_5H_3NH^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	3.47	-4				*	(11)
.42	$C_2H_5NO_2 + \overline{C_6H_4CH{:}CHCH{:}N} \longrightarrow$ (quinoline) $CH_3CH{:}NO_2^- + \overline{C_6H_4CH{:}CHCH{:}NH}^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	7.5	-5				*	(11)
.43	$C_2H_5NO_2 + \overline{C_6H_4CH{:}CHN{:}CH} \longrightarrow$ (isoquinoline) $CH_3CH{:}NO_2^- + \overline{C_6H_4CH{:}CHNH{:}CH}^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	1.27	-4				*	(11)
.44	$C_2H_5NO_2 + \overline{C_6H_4CH{:}CHC(CH_3){:}N} \longrightarrow$ (2-methyl quinoline) $CH_3CH{:}NO_2^- + \overline{C_6H_4CH{:}CHC(CH_3){:}NH}^+$	Et 30*	A = 0.1-0.2; B = 0.1-0.2	I_2	0.002-0.004	k AB	25	1.28	-4				*	(11)
.45	$CH_3CHClNO_2 + H_2O \longrightarrow$ $CH_3CCl{:}NO_2^- + H_3O^+$	B		Br_2	> A and < A	k A	35	1.05	-6					(3)
							35	1.7	-6					(8)
							48	6.2	-6	20	3	8		
.46	$C_6H_2(NO_2)_3CH_3 + C_2H_5O^- \longrightarrow$ $C_6H_2(NO_2)_3{:}CH_2^- + C_2H_5OH$	M				k AB	-78	4.58	-4					(2)
							-70	2.18	-3					
							-60	1.00	-2					
							-50	4.42	-2					
							-40	1.64	-1					
							-30	5.61	-1					
							19	6.30	+1	13.6	1.0	12		

Supplement 1958

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Two activating groups C:O and NO_2													
.47	$CH_3COCH_2NO_2 + H_2O \longrightarrow CH_3COCNO_2^- + H_3O^+$	B		Br_2	> A	k A	0	2.0	-3					(8)
							10	6.4	-3	19	3	12		
.48	$NO_2CH_2COOC_2H_5 + H_2O \longrightarrow NO_2CHCOOC_2H_5^- + H_3O^+$	B		Br_2	> A	k A	0	5.3	-4					(8)
							10	1.52	-3	16	3	9		
	Two NO_2 activating groups													
.49	$CH_2(NO_2)_2 + H_2O \longrightarrow CH(NO_2)_2^- + H_3O^+$	B		Br_2	> A	k A	0	4.5	-2					(8)
	Two C:O activating groups													
.50	$CH_3COCH(CH_3)COCH_3 + H_2O \longrightarrow$ $CH_3COC(CH_3)COCH_3^- + H_3O^+$	B	A = 0.033	Br_2	0.003	k A	21	5.8	-5					(9)
							25	8.3	-5					
							35	2.3	-4	18	1.2	9		
.51	$CH_3COCH_2COCF_3 + H_2O \longrightarrow$ $CH_3COCHCOCF_3^- + H_3O^+$	Et 12*	10^2A = 4-8	Br_2	0.04-0.08	k A	0	8.99	-4					(13)
							14	4.65	-3					
							25	1.57	-2	19.7	4	13		
			M = 0.1-0.5				25	1.48	-2					
		Et 16*					25	1.49	-2					
		Et 33*					25	1.37	-2					
		Et 50*					25	1.37	-2					
		Et 67*					25	1.26	-2					
		Et 83*					25	9.27	-3					
		Et 95*					25	6.44	-3					
.52	$(CH_3)_2CHCH_2COCH_2COCF_3 + H_2O \longrightarrow$ $(CH_3)_2CHCH_2COCHCOCF_3^- + H_3O^+$	Et 6*	A = 0.01	Br_2	0.014	k A	14	3.42	-3					(13)
							25	1.18	-2	19	1	12		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.53	$C_6H_5COCH_2COCF_3 + H_2O \longrightarrow C_6H_5COCHCOCF_3^- + H_3O^+$	Et 4*	$A \simeq 0.01$	Br_2	0.008	k A	14 25	3.72 8.55	-3 -3	13	3	7		(13)
.54	$\overline{SCH:CHCH:C}COCH_2COCF_3 + H_2O \longrightarrow$ $\overline{SCH:CHCH:C}COCHCOCF_3^- + H_3O^+$	Et 10*	$A \simeq 0.01$	Br_2	~0.01	k A	14 25	2.96 1.01	-3 -2	19	7	11		(13)
.55	$CH_3COCH(C_2H_5)COOC_2H_5 + H_2O \longrightarrow$ $CH_3COC(C_2H_5)COOC_2H_5^- + H_3O^+$	B	$10^2A = 3$	Br_2	0.001	k A	20 25 35	4.8 7.6 1.73	-6 -6 -5	15.5	1.6	6		(9)
.56	$(C_2H_5OOC)_2CH_2 + H_2O \longrightarrow (C_2H_5OOC)_2CH^- + H_3O^+$	B	$10^3A = 5\text{-}25$	Br_2	0.001-0.003	k A	25	3.0	-5					(9)
.57	$(C_2H_5OOC)_2CBrH + H_2O \longrightarrow (C_2H_5OOC)_2CBr^- + H_3O^+$	B	$10^3A = 1\text{-}4$	Br_2	0.0001-0.003	k A	25	1.4	-4					(9)
	Activating groups C:O and C⋮N													
.58	$C_2H_5OOCCH_2CN + H_2O \longrightarrow C_2H_5OOCCHCN^- + H_3O^+$	B		Br_2	> A	k A	0 10	7.1 2.3	-5 -4	17	2	9		(8)
.59	$C_2H_5OOCCHBrCN + H_2O \longrightarrow C_2H_5OOCCBrCN^- + H_3O^+$	B		Br_2	> A	k A	0	8	-2					(8)
	Two C⋮N activating groups													
.60	$(CN)_2CH_2 + H_2O \longrightarrow (CN)_2CH^- + H_3O^+$	B	$10^3A = 2\text{-}3$	Br_2	0.006-0.02	k A	0 10	1.00 2.9	-3 -3	18	2	11		(8)
.61	$(CN)_2CBrH + H_2O \longrightarrow (CN)_2CBr^- + H_3O^+$	B		Br_2	> A	k A	0	>> 2	-1					(8)
	Two Aryl and a C:OO⁻ activating groups													
.62	$p\text{-}CH_3C_6H_4(C_6H_5)CHCOO^- + OH^- \longrightarrow$ $p\text{-}CH_3C_6H_4(C_6H_5)CCOO^= + H_2O$	B	A = 0.2; B = 0.2	D_2O	3%	k A	100	6.4	-6					(4)

CODED SOLVENTS

Et 30*(70) C_2H_5OH vol % indicated + H_2O

COMMENTS

General. Ionization assumed to be rate controlling step in halogenation and enolization reactions. For additional reactions under these categories see 312.471 and 112.440. For reverse reactions see 622.450.

Methods: Polarography (4)

Hydrogen-deuterium exchange (3)

Substitution (halogenation) (7) (8) (10) (11) (12)

Conductometric (7) (8) (10) (11)

Thermal Maximum (1)

Steady State, while introducing "B" at controlled rate (9)

Spectrophotometric (2)

Reactions: **(.24)** Values of (4) include reaction with base of buffer but actual concentration of buffer not stated. **(.25)** Selected data of (1) who use reaction rates to calculate dissociation constants of such bases as $CaOH^+$, $BaOH^+$ and TlOH based on the assumption that OH^- is the only base reacting. **(.26)-(.36)** Simultaneous reaction with OH^-, (.25) corrected for. Integrated form of rate equation used was:

$$t = \frac{k_3K_b}{(ak + K_bk_3)^2} \ln \frac{a-x}{kx + k_3K_b} + \frac{a}{(ak + k_3K_b)(a-x)} + C$$

Where. k_3 = independently determined rate constant for (.25). K_b = ionization constant of amine, "a" = initial concentration of A and x = amount of A reacted at time t. **(.37)-(.44)** Simultaneous reaction, (.25), with OH^- eliminated by addition of drop of strong acid. Amount shown to be not critical.

LITERATURE

(1) R.P. Bell, M.H. Panckhurst, *CSL* **1956**, 2836. (2) E.F. Caldin, G. Long, F.W. Trowse, *Nature* 1953, **171**, 1124. (3) M.F. Hawthorne, R.D. Strahm, *ACS* 1957, **79**, 3471. (4) D.J.G. Ives, G.C. Wilks, *CSL* **1938**, 1455. (5) Junell, *Arkiv. Kemi. Mineral. Geol.* 1934, **11B**, 30. (6) E.W. Miller, A.P. Arnold, M.J. Astle, *ACS* 1948, **70**, 3971. (7) R.G. Pearson, *J.C.P.* 1952, **20**, 1478. (8) R.G. Pearson, R.L. Dillon, *ACS* 1953, **75**, 2439. (9) R.G. Pearson, J.M. Mills, *ACS* 1950, **72**, 1692. (10) R.G. Pearson, L.H. Piette, *ACS* 1954, **76**, 3087. (11) R.G. Pearson, F.V. Williams, *ACS* 1953, **75**, 3073. (12) R.G. Pearson, F.V. Williams, *ACS* 1954, **76**, 258. (13) J.C. Reid, M. Calvin, *ACS* 1950, **72**, 2948.

ELIMINATION

Bond Unsaturation

Elimination of C_5H_5N and H^+ to form C:C

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $>CH-C<\ (+NC_5H_5) + OH^- \longrightarrow >C{:}C< + C_5H_5N + H_2O$

Rate measured: $-dB/dt$

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
.1	$n\text{-}C_4H_9CH(\overset{+}{N}C_5H_5)CH_2SO_3^- + OH^- \longrightarrow n\text{-}C_4H_9CH{:}CHSO_3^- + C_5H_5N + H_2O$ [2-(1-proto-1-pyridyl)-1-hexanesulfonate]	H_2O	A=0.02; B=0.02-0.04	k AB	65	1.28	-5	
.2	$C_6H_5CH(\overset{+}{N}C_5H_5)CH_2SO_3^- + OH^- \longrightarrow C_6H_5CH{:}CHSO_3^- + C_5H_5N + H_2O$ [2-phenyl-2-(1-proto-1-pyridyl)-1-ethanesulfonate]	H_2O	A = B = 0.02	k AB	20	1.0	-3	
.3	*trans*-$\overbrace{CH_2CH_2CH_2CH(\overset{+}{N}C_5H_5)}CHSO_3^- + OH^- \longrightarrow \overbrace{CH_2CH_2CH_2CH{:}}CSO_3^- + C_5H_5N + H_2O$ [*trans*-2-(1-proto-1-pyridyl)-1-cyclopentane sulfonate]	H_2O	A = B = 0.02	k A^3	99	6.0	-2	*

COMMENTS

Reaction. (.3) Rate law with respect to each reactant not determined as A = B. Calculated third order constant gave best fit for the single determination. The *cis*-isomer reacted very slowly except in presence of Ba^{++} where a slight autocatalysis was observed leading to a steady zero order rate, possibly due to catalysis at surface of precipitating Barium sulfonate.

LITERATURE

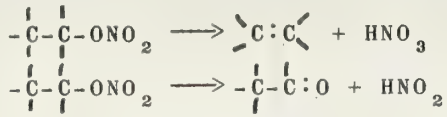
F.G. Bordwell, M.L. Peterson, *ACS* 1955, **77**, 1145.

ELIMINATION

Double bond formation by elimination from nitrate ester

Liquid phase

Reaction types:



Amounts are in M/l. Rate constants are in M/l and sec.

Coded solvents at end of table.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C_2H_5ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow CH_2{:}CH_2 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_3^-$	Et 90*	$10^2A = 3$; $10^2B = 9$			k AB	30	6	-8				*	(1)
							59	8	-7					
		Et 60*					60	4	-8					
.2	$C_2H_5ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow CH_3CH{:}O + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A = 3$; $10^2B = 9$			k AB	30	3	-8				*	(1)
							59	2.1	-6					
		Et 60*					45	4	-8					
							60	2.4	-7					
.3	$(CH_3)_2CHONO_2 \longrightarrow (CH_3)_2C{:}O + HNO_2$	Et 90*	$10^2A = 3$			k A	75	3	-9				*	(1)
.4	$(CH_3)_2CHONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $CH_3CH{:}CH_2 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_3^-$	Et 90*	$10^2A = 3$; $10^2B = 9$			k AB	59	9	-7				*	(1)
							80	7.2	-6					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.5	$(CH_3)_2CHONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$	Et 90*	$10^2A = 3$; $10^2B = 9$			k AB	59	9	-7				*	(1)
							80	5.5	-6					
		Et 60*					60	3	-7					
	$(CH_3)_2C{:}O + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$													
.6	$(CH_3)_3CONO_2 \longrightarrow (CH_3)_2C{:}CH_2 + H^+ + NO_3^-$	Et 90*	$10^2A = 2$-5			k A	0	3.3	-7				*	(1)
							20	5.6	-6					
							30	2.38	-5	23.5				
		Et 90*	$10^2A = 2$-4	NaOH	0.088	k A	0	6	-7					
							20	1.54	-5					
							30	5.5	-5	25.4				
		Et 60*	$10^2A = 3$-4			k A	0	8.0	-6					
							10	3.9	-5					
							30	5.19	-4	23.0				
				NaOH	0.087		0	1.1	-5					
					0.10		9	4.95	-5					
					0.11		20	2.94	-4	25.6				
		DW 95*	$10^2A = 6$-14			k A	25	6	-7				*	(6)
		DW 85*					25	5.1	-6					
		DW 75*					25	1.7	-5					
		DW 60*					0	2.2	-6					
							10	1.0	-5	25				
				$NaClO_4$	0.1		0	2.5	-6					
					0.1		10	1.2	-5					
				NaOH	0.1		10	1.1	-5					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.7	$C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CHO + HNO_2$	C_2H_5OH		C_6H_5OH	0	k A	60	1.19	-6				*	(4)
					1.0		60	1.27	-6					
		DW 60*	10^2A = 13				25	5.6	-9					(6)
			11				50	9.8	-8	24.2				
			15	$NaClO_4$	0.11		25	5.2	-9					
			8		0.11		50	1.37	-7					
.8	$C_6H_5CH_2ONO_2 + C_2H_5O^- \longrightarrow C_6H_5CHO + C_2H_5OH + NO_2^-$	C_2H_5OH	$10^2A = 4$; $B = 0.10$			k AB	60	1.34	-2				*	(4)
.9	$C_6H_5CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow C_6H_5CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A = 3\text{-}5$; $10^2B = 3\text{-}10$			k AB	20	9.24	-5				*	(2)
							30	3.16	-4					
							45	1.75	-3					
							60	8.47	-3	21.8	1.9	12		
		Et 60*				k AB	20	2.45	-5					
							30	7.90	-5					
							45	4.10	-4					
							60	1.90	-3	20.9	1	11		(2) (4)
		Et 45*	$10^2A = 4$; $B = 0.1$			k AB	60	9.8	-5					(4) (5)
				$CO_3^=$	.03		60	7	-5					(5)
				$C_6H_5O^-$	.03		60	9	-5					(5)
.10	$C_6H_5CH_2ONO_2 + C_6H_5O^- \longrightarrow C_6H_5CHO + C_6H_5OH + NO_2^-$	C_2H_5OH	$10^2A = 5\text{-}9$; $10^2B = 3\text{-}21$	C_6H_5OH	.030	k AB	45	3.8-3.4	-5				*	(3) (4)
					.046		45	2.72	-5					
					.090		45	1.77	-5					
					.21		45	1.08	-5					
					∞		45	7	-6					
					0.006		60	4.9-3.6	-4					
					0.025		60	2.7-2.2	-4					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.10	$C_6H_5CH_2ONO_2 + C_6H_5O^- \longrightarrow$ *(continued)*	C_2H_5OH	10^2A = 5-9; 10^2B=3-21	C_6H_5OH	0.067	k AB	60	1.28	-4				*	([3]) ([4])
					0.10		60	9.9	-5					
					0.23		60	6.3	-5					
					0.72		60	2.97	-5					
					∞		60	3.80	-5					
.11	$C_6H_5CH\ ONO_2 + p\text{-}CH_3OC_6H_4O^- \longrightarrow$ $C_6H_5CHO + p\text{-}CH_3OC_6H_4OH + NO_2^-$	C_2H_5OH	10^2A = 5-6; B = 0.10	M	0.002	k AB	60	9.9-7.4	-4				*	([4])
					0.038		60	3.4-3.2	-4					
					0.062		60	2.35	-4					
					0.097		60	1.77	-4					
					0.20		60	1.11	-4					
					0.50		60	6.38	-5					
					∞		60	5.63	-5					
.12	$C_6H_5CH_2ONO_2 + m\text{-}NO_2C_6H_4O^- \longrightarrow$ $C_6H_5CHO + m\text{-}NO_2C_6H_4OH + NO_2^-$	C_2H_5OH	10^2A = 5; 10^2B = 9-10	M	0.001	k AB	60	2.4-1.6	-5				*	([4])
					0.16		60	5.84	-6					
					0.26		60	4.40	-6					
					0.41		60	3.60	-6					
					1.00		60	1.43	-6					
					∞		60	2.2	-6					
.13	$C_6H_5CH_2ONO_2 + p\text{-}NO_2C_6H_4O^- \longrightarrow$ $C_6H_5CHO + p\text{-}NO_2C_6H_4OH + NO_2^-$	C_2H_5OH	10^2A = 5-6; B = 0.1	M	0	k AB	60	2.0-1.5	-6				*	([4]) ([5])
					0.063		60	1.22	-6					
					0.096		60	1.08	-6					
					0.19		60	1.00	-6					
					0.39		60	7.6	-7					
					∞		60	8.5	-7					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.14	$p\text{-}CH_3C_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $p\text{-}CH_3C_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A = 3\text{-}5$; $10^2B = 3\text{-}10$			k AB	20	2.90	-5				*	([2])
							30	9.85	-5					
							45	6.15	-4					
							60	3.06	-3	22.6	1.9	12		
		Et 60*					20	8.66	-6					
							30	2.99	-5					
							45	1.50	-4					
							60	7.42	-4	21.2	6	10		
.15	$p\text{-}CH_3OC_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $p\text{-}CH_3OC_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	20	1.91	-5				*	([2])
.16	$o\text{-}NO_2C_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $o\text{-}NO_2C_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	0	2.44	-1				*	([2])
		Et 60*					0	5.18	-2					
.17	$m\text{-}NO_2C_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $m\text{-}NO_2C_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	-10	8.74	-4				*	([2])
							0	3.65	-3					
							10	1.31	-2					
							20	4.56	-2	20.6	1.3	14		
		Et 60*					0	9.19	-4					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.18	$p\text{-}NO_2C_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $p\text{-}NO_2C_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	-10	1.01	-1				*	([2])
							0	3.48	-1					
							10	1.06	0	17.9	8	13		
		Et 60*					0	7.4	-2					
.19	$p\text{-}BrC_6H_4CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $p\text{-}BrC_6H_4CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	20	8.54	-4				*	([2])
		Et 60*					20	2.04	-4					
.20	$C_6H_5CH_2CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $C_6H_5CH{:}CH_2 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_3^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	60	8.1	-5				*	([2])
.21	$C_6H_5CH_2CH_2ONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow$ $C_6H_5CH_2CHO + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$			k AB	60	3.3	-6				*	([2])

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.22	$C_6H_5(CH_3)CHONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow C_6H_5CH{:}CH_2 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_3^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$	k AB	20	1.6	-7				*	(2)
.23	$C_6H_5(CH_3)CHONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow C_6H_5(CH_3)C{:}O + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$	k AB	20	1.27	-6				*	(2)
.24	$(C_6H_5)_2CHONO_2 + C_2H_5O^- \longrightarrow (C_6H_5)_2C{:}O + C_2H_5OH + NO_2^-$	C_2H_5OH	$10^2A \sim 3$; $10^2B \sim 5$	k AB	10 20 30	1.61 5.25 1.59	-4 -4 -3	19.5	2	11	*	(2)
.25	$(C_6H_5)_2CHONO_2 + \begin{cases} OH^- \\ C_2H_5O^- \end{cases} \longrightarrow (C_6H_5)_2C{:}O + \begin{cases} H_2O \\ C_2H_5OH \end{cases} + NO_2^-$	Et 90*	$10^2A \sim 3$; $10^2B \sim 5$	k AB	0 10 20	2.98 1.07 3.17	-5 -4 -4	19.0	5	10		(2)

SOLVENTS

Et 90* (60) (45) — C_2H_5OH vol % indicated + H_2O (1) (2) (4) (5)

DW 95* (85) (75) (60) — Dioxane wt % indicated + H_2O (6)

Supplement 1958

COMMENTS

General. In aqueous and alcoholic solutions elimination reactions occur simultaneously with solvolysis reactions which lead to the formation of corresponding alcohols and ether. For these reactions see 212.451. Elimination may simultaneously lead to two types of products, *(a)* formation of olefin by loss of H^+ and NO_3^-, *(b)* the formation of aldehyde or ketone by elimination of H^+ and NO_2^-. The total reaction involving solvolysis and elimination has been broken up into the individual reactions by determinations of the amount of olefin, nitrite and the total base consumed.

Reactions. **(.1) (.2)** Reactions occur simultaneously and are assumed to be of the same order. **(.3)** Extent of olefin formation not indicated. **(.4) (.5)** Reactions occur simultaneously and are assumed to be of the same order. **(.6)** First order rate law observed and even addition of strong base, OH^-, did not appear to increase rate more than observed with salts. Values given by ([6]) are for initial rate since calculated first order constants tended to increase with the course of reaction in dioxane solutions. **(.7)** In absence of strong base first order rate law valid. Values listed by ([6]) in dioxane solutions are initial rates as calculated constants increased slightly with course of reaction. **(.8)** Negligible solvolysis observed. **(.9)** Elimination reaction observed by ([2]) to make up 87% of total reaction. **(.10) (.11) (.12) (.13)** Total rate observed is composite of reaction due to $C_6H_5O^-$ and $C_2H_5O^-$. Addition of C_6H_5OH shifted the equilibrium from $C_2H_5O^-$ to $C_6H_5O^-$ and C_2H_5OH. Value listed under ∞ of C_6H_5OH obtained by extrapolation to value of k for $[C_6H_5O^-]^{-1} = 0$. At high phenol concentrations abnormally large decreases in k were observed which were neglected in making the extrapolations. **(.14)** Elimination observed to represent 54% of total reaction. **(.15)** Reaction is predominantly solvolysis and elimination accounts for only 0.2% of total reaction. **(.16)** No observable solvolysis and elimination accounts for 100% of total reaction. **(.17) (.18) (.19)** Elimination accounts for 96% of total reaction. **(.20) (.21)** Reactions occur simultaneously and are assumed to be of the same order. **(.22) (.23)** Reactions occur simultaneously and are assumed to be of the same order. **(.24)** Elimination accounts for only 1% of total reaction.

LITERATURE

(1) J.W. Baker, D.W. Easty, *CSL* **1952,** 1208.

(2) J.W. Baker, T.G. Heggs, *CSL* **1955,** 616.

(3) J.W. Baker, A.J. Neale, *NAT* 1953, **172,** 583.

(4) J.W. Baker, A.J. Neale, *CSL* **1954,** 3225.

(5) J.W. Baker, A.J. Neale, *CSL* **1955,** 608.

(6) G.R. Lucas, L.P. Hammett, *ACS* 1942, **64,** 1928.

ELIMINATION

Bond Unsaturation

Elimination of NO_3^- and halide ion to form C:C

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Reaction type: $>C(X)-C(ONO_2)< + 3I^- \longrightarrow >C=C< + X^- + NO_3^- + I_3^-$

Rate measured: $+dO/dt$

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	*cis*-$CH_2CH_2CH_2CH_2CHBrCHONO_2 + 3I^- \longrightarrow$ *cyclo*-$C_6H_{10} + Br^- + NO_3^- + I_3^-$	n-C_3H_7OH	$10^2A = 2.6$-3; B = 0.2-0.23	k AB	88 116	1.60 3.80	-6 -5	32	4	13
.2	*trans*-$CH_2CH_2CH_2CH_2CHBrCHONO_2 + 3I^- \longrightarrow$ *cyclo*-$C_6H_{10} + Br^- + NO_3^- + I_3^-$	n-C_3H_7OH	$10^2A = 2$-3; B = 0.2-0.23	k AB	88 116	1.50 3.79	-6 -5	32	4	13

COMMENTS

Calculated rate constants decreased with progress of reaction but authors state that the second order constants did not vary with variation of initial concentrations of A and B.-Rate constants apply to first 20% of reaction.

LITERATURE

S.J. Cristol, J.Q. Weber, M.C. Brindell, *ACS* 1956, **78**, 598.

ELIMINATION

Bond-unsaturation elimination

Thio ether and H^+ from alkyl sulfonium ion

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents at end of table.

For simultaneous solvolysis reactions see 242.461. Reaction measured $+dL/dt$ unless stated otherwise.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$(CH_3)_2SC_2H_5^+ + C_2H_5O^- \longrightarrow CH_2{:}CH_2 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	45 64	5.0 6.0	-5 -4	28	9	14	*	(5)
.2	$(CH_3)_2SCH_2CH_2CH_3^+ + C_2H_5O^- \longrightarrow CH_2{:}CHCH_3 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	64	2.7	-4				*	(5)
.3	$(CH_3)_2SCH(CH_3)_2^+ + C_2H_5O^- \longrightarrow CH_3CH{:}CH_2 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	45 64	1.14 1.04	-3 -2	25	2	14	*	(6)
.4	$(CH_3)_2SCH_2CH_2CH_2CH_3^+ + C_2H_5O^- \longrightarrow$ $\longrightarrow CH_2{:}CHCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	64	1.7	-4				*	(5)
.5	$(CH_3)_2SCH_2CH(CH_3)_2^+ + C_2H_5O^- \longrightarrow$ $\longrightarrow CH_2{:}C(CH_3)_2 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	64	1.4	-4				*	(5)
.6	$(CH_3)_2SCH(CH_3)C_2H_5^+ + C_2H_5O^- \longrightarrow \left\{\begin{matrix} CH_2{:}CHC_2H_5 \\ CH_3CH{:}CHCH_3 \end{matrix}\right\} + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A= 0.05; B= 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	64	6.9	-3				*	(6)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.7	$(CH_3)_2SC(CH_3)_3^+ \longrightarrow CH_2{:}C(CH_3)_2 + (CH_3)_2S + H^+$ ↘ (solvolysis)	Et 97*	A = 0.02-0.03	I^-	= A	$dL/dt = k\,A$	50	9.0	-6				*	(7)
.8	$(CH_3)_2SC(CH_3)_3^+ + C_2H_5O^- \longrightarrow CH_2{:}C(CH_3)_2 + (CH_3)_2S + C_2H_5OH$	C_2H_5OH	A = 0.02; B = 0.1	I^-	= A	$k\,AB$	20	1.14	-3				*	(2)
				Na^+	= B		45	2.93	-2	24	8	14		
		Et 97*	A = 0.02-0.05;	I^-	= A		24	7-8	-2					(7)
			B = 0.3-0.5	Na^+	= B									
.9	$(CH_3)_2SC(CH_3)_2C_2H_5^+ \longrightarrow CH_2{:}C(CH_3)C_2H_5 + (CH_3)_2S + H^+$ ↘ (solvolysis)	Et 97*	A = 0.02-0.12	I^-	= A	$k\,A$	50	9.7	-5				*(1) (2) (7)	
		Et 80*					50	3.18	-5					(1)(2)
							65	3.05	-4					
							83	3.29	-3	32.1	1.7	17		
		Et 50*					65	1.80	-4					
.10	$(CH_3)_2SC(CH_3)_2C_2H_5^+ + C_2H_5O^- \longrightarrow$ $\longrightarrow \left\{\begin{matrix} CH_2{:}C(CH_3)C_2H_5 \\ CH_3CH{:}C(CH_3)_2 \end{matrix}\right\} + (CH_3)_2S + C_2H_5OH$	Et 97*	A = 0.05-0.09;	I^-	= A	$k\,AB$	24	5-6	-4				*	(7)
			B = 0.2-0.4	Na^+	= B									
.11	$(CH_3)_2SCH_2CH_2C_6H_5^+ + OH^- \longrightarrow CH_2{:}CHC_6H_5 + (CH_3)_2S + H_2O$ ↘ (solvolysis)	H_2O	A = B = 0.1	Br^-	= A	$-dB/dt = k\,AB$	41	1.30	-5				*	(8)
				Na^+	= B		59	1.14	-4					
							71	4.32	-4	24.8	2	12		
.12	$(CH_3)_2SCH_2CH_2C_6H_5^+ + C_2H_5O^- \longrightarrow$ $\longrightarrow CH_2{:}CHC_6H_5 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A = 0.06; B = 0.1	I^-	= A	$-dB/dt = k\,AB$	30	3.79	-3				*	(3)
			0.05 0.1	Na^+	= B		35	1.05	-2					(5)
							46	3.98	-2	24	1.0	15		

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.13	$(CH_3)_2SCH(CH_3)C_6H_5^+ + C_2H_5O^- \longrightarrow CH_2{:}CHC_6H_5 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = k\,AB$	64	5.78	-2	*	(6)
.14	$(CH_3)_2SCH_2CH_2C_6H_4\text{-}p\text{-}CH_3 + C_2H_5O^- \longrightarrow p\text{-}CH_3C_6H_4CH{:}CH_2 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A = 0.06; B = 0.1	I^- Na^+	= A = B	$-dB/dt = k\,AB$	30	9.13	-4	*	(3)
.15	$(CH_3)_2SCH_2CH_2C_6H_4\text{-}p\text{-}Cl + C_2H_5O^- \longrightarrow p\text{-}ClC_6H_4CH{:}CH_2 + (CH_3)_2S + C_2H_5OH$ ↘ (solvolysis)	C_2H_5OH	A = 0.06; B = 0.1	I^- Na^+	= A = B	$-dB/dt = k\,AB$	30	2.18	-2	*	(3)
.16	$(C_2H_5)_3S^+ + OH^- \longrightarrow CH_2{:}CH_2 + (C_2H_5)_2S + H_2O$ ↘ (solvolysis)	H_2O	A = 0.2-0.4; B = 0.2-0.7	Na^+	= B	$dL/dt = k\,AB$	100	2.4	-5	*	(4)
		Et 80*	A = B = 0.15				100	2.05	-2		
		Et 60*	A = 0.2; B = 0.2-0.4				100	2.10	-3		
.17	$CH_3S[CH(CH_3)_2]_2^+ + OH^- \longrightarrow CH_2{:}CHCH_3 + CH_3SCH(CH_3)_2 + H_2O$	Et 60*	A = 0.1; B = 0.1-0.2	Na^+	= B	$dL/dt = k\,AB$	100	1.88	-3	*	(4)

CODED SOLVENTS

Et 97*	C_2H_5OH + 2.8 wt. % H_2O (97 vol. % C_2H_5OH)
Et 80*	C_2H_5OH 80 vol. % + H_2O 20 vol. %
Et 60*	C_2H_5OH 60 vol. % + H_2O 40 vol. %
Et 50*	C_2H_5OH 50 vol. % + H_2O 50 vol. %

COMMENTS

General. Reactants are listed in the order of increasing complexity. First are dimethyl sulfonium salts in the order of increasing numbers of C atoms of the third alkyl group. Straight chain isomers precede the branched-chain isomers. The dimethyl sulfonium salts are followed by diethyl, etc. In almost all cases the elimination is accompanied by a parallel solvolysis reaction which in some cases may be the predominant reaction. Both reactions appear to be of the same order. These are listed together with a rate constant $k = k_E + k_S$ in table 242.461. In this table the derived rate constant for the elimination reaction only is listed. This constant has been calculated from the overall constant by multiplying k by the fraction of olefin found in the reaction products.

Reaction. **(.1)** Elimination accounts for 12% and 15.4% of the total reaction at 45 and 64°C respectively. **(.2)** Elimination accounts for 7.1% of total reaction. **(.3)** Elimination accounts for 61 and 65.7% of the total reaction at 45 and 64°C respectively. **(.4)** Elimination accounts for 4.3% of the total reaction. **(.5)** Elimination accounts for 2.4% of the total reaction. **(.6)** Elimination accounts for 57.7% of total reaction with 74% of olefin as $CH_2{:}CHC_2H_5$ and 26% as $CH_3CH{:}CHCH_3$. **(.7)** Elimination accounts for 50.5% of the total reaction. **(.8)** Parallel solvolysis reaction negligible and amounts to less than 1% of total reaction. **(.9)** Elimination accounts for 64.4% and 39.8% of total reaction in the 97 vol % and 50 vol % ethanol respectively. In 80 vol % ethanol elimination accounts for 47.8%, 49.4% and 53.7% of the total reaction at 50°, 65°, and 83°C respectively. A slight decrease in olefin % with course of reaction is probably due to a consecutive solvolysis of the olefin. **(.10)** Elimination accounts for 96-98% of total reaction. Olefin consists of 86% of $CH_2{:}C(CH_3)C_2H_5$ and 14% of $CH_3CH{:}C(CH_3)_2$. Second order rate law followed for 90% of reaction course but calculated constants showed slight decrease with increase in B. **(.11)** Extent of parallel solvolysis reaction not stated. At 59°C isotope effect S^{32}/S^{34} is + 0.15%. **(.12)** At 64°C elimination accounts for 89.4% of total reaction. **(.13)** Elimination accounts for 59.1% of total reaction at 64°C. Rate constant extrapolated to 64°C from 20° and 45°. **(.14)** **(.15)** Extent of parallel solvolysis reaction not determined and rate constant given is for total reaction, elimination and solvolysis. **(.16)** Elimination accounts for 86% of total reaction in H_2O and 100% in the ethanol water mixtures. **(.17)** No appreciable solvolysis reaction in contrast to this reaction in H_2O where no appreciable olefin formation is observed and reaction obeys first order kinetics.

LITERATURE

(1) K. A. Cooper, M.L. Dhar, E.D. Hughes, C.K. Ingold, B.J. MacNulty, *CSL* **1948,** 2043. (2) K. A. Cooper, E.D. Hughes, C.K. Ingold, G.A. Maw, B.J. MacNulty, *CSL* **1948,** 2049. (3) C.H. DePuy, D.H. Froemsdorf, *ACS* 1957, **79,** 3710. (4) J.L. Gleave, E.D. Hughes, C.K. Ingold, *CSL* **1935,** 236. (5) E.D. Hughes, C.K. Ingold, G.A. Maw, *CSL* **1948,** 2072. (6) E.D. Hughes, C.K. Ingold, G.A. Maw, L.I. Woolf, *CSL* **1948,** 2077. (7) E.D. Hughes, C.K. Ingold, L.I. Woolf, *CSL* **1948,** 2084. (8) W.H. Saunders, S. Asperger, *ACS* 1957, **79,** 1612.

ELIMINATION

Bond-unsaturation elimination

Aryl sulfonic acid from Alkyl arylsulfonate

$$\underset{(A)}{R_1R_2CHCHR_3OSO_2Ar} \longrightarrow \underset{(L)}{\begin{cases} R_1R_2C{:}CHR_3 \\ R_1R_2CHCH{:}R_3 \end{cases}} + \underset{(M)}{ArSO_3H}$$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

Coded solvents at end of Table.

For parallel ester exchange see 222.461

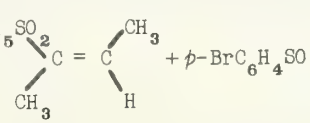
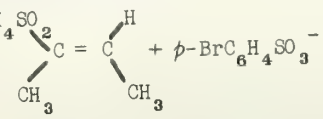
Rate measured dM/dt unless otherwise indicated

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_2H_5(CH_3)CHOSO_2C_6H_4\text{-}p\text{-}CH_3 \longrightarrow$	CH_3COOH	$A \simeq 0.6$			$dL/dt = k'A$	60	5	-6	*	(7)
				CH_3COONa	0.1		65	2	-5		
	$\longrightarrow \begin{Bmatrix} CH_2{:}CHCH_2CH_3 \\ CH_3CH{:}CHCH_3 \end{Bmatrix} + p\text{-}CH_3C_6H_4SO_3H$ k'										
	$\longrightarrow$ (ester exchange) k''										
.2	$C_2H_5(CH_3)CHOSO_2C_6H_4\text{-}p\text{-}Br \longrightarrow$	Ac*	$A \sim 0.03$			$-dA/dt = (k' + k'')A$	70	1.29	-4	*	(4)
	$\longrightarrow \begin{Bmatrix} CH_2{:}CHCH_2CH_3 \\ CH_3CH{:}CHCH_3 \end{Bmatrix} + p\text{-}BrC_6H_4SO_3H$ k'										
	$\longrightarrow$ (ester exchange) k''										
.3	$n\text{-}C_3H_7(CH_3)CHOSO_2C_6H_4\text{-}p\text{-}Br \longrightarrow$	Ac*	$A \sim 0.03$			$dL/dt = k'A$	70	3.9	-5	*	(4)
						$-dA/dt = (k' + k'')A$	70	1.23	-4		
	$\longrightarrow \begin{Bmatrix} n\text{-}C_3H_7CH{:}CH_2 \\ C_2H_5CH{:}CHCH_3 \end{Bmatrix} + p\text{-}BrC_6H_4SO_3H$ k'										
	$\longrightarrow$ (ester exchange) k''										

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.4	$(CH_3)_2CHCH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}Br \longrightarrow$	Ac*	A ~ 0.03			$dL/dt = k'A$	70	5.3	-5		*	([4])
	$\longrightarrow \left\{\begin{matrix}(CH_3)_2CHCH{:}CHCH_3 \\ (CH_3)_2CHCH_2CH{:}CH_2\end{matrix}\right\} + p\text{-}BrC_6H_4SO_3H$ k'					$-dA/dt = (k' + k'')A$	70	1.13	-4			
	$\longrightarrow$ (ester exchange) k''											
.5	$(CH_3)_3CCH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}Br \longrightarrow$	Ac*	A ~ 0.03			$dL/dt = k'A$	70	1.8	-4		*	([4])
	$\longrightarrow \left\{\begin{matrix}(CH_3)_3CCH_2CH{:}CH_2 \\ (CH_3)_3CCH{:}CHCH_3\end{matrix}\right\} + p\text{-}BrC_6H_4SO_3H$ k'					$-dA/dt = (k' + k'')A$	70	2.64	-4			
	$\longrightarrow$ (ester exchange) k''											
	Cyclic-arylsulfonate											
.6	$\overline{CH_2CH_2CH_2CH_2}CHOSO_2C_6H_4\text{-}p\text{-}CH_3 \longrightarrow$	Acl*	A = 0.1	CH_3COOK	0.1	$dL/dt = k'A$	50	1.80	-5		*	([8])
	$\longrightarrow \overline{CH_2CH_2CH_2CH{:}CH} + p\text{-}CH_3C_6H_4SO_3H$ k'		0.5		0.5		50	2.8	-5			
			0.1		0.1		55	3.5	-5			
	$\longrightarrow$ (ester exchange) k''		0.1		0.1		60	6.2	-5	28		
			0.1		0.1	$(k' + k'')A$	60	1.6	-4			
.7	$\overline{CH_2(CH_2)_4}CHOSO_2C_6H_4\text{-}p\text{-}CH_3 \longrightarrow$	Acl*	A = 0.1	CH_3COOK	0.1	$dL/dt = k'A$	75	5.1	-5		*	([8])
	$\longrightarrow \overline{CH_2(CH_2)_3CH{:}CH} + p\text{-}CH_3C_6H_4SO_3H$ k'		0.5		0.5		75	9.3	-5			
			0.1		0.1		80	9.1	-5			
	$\longrightarrow$ (ester exchange) k''		0.1		0.1		85	1.55	-4			
			0.1		0.1	$(k' + k'')A$	85	1.82	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
	Aryl-substituted-alkyl-arylsulfonates										
.8	$C_6H_5CH_2CH_2OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.06;			$-dA/dt = (k' + k'')AB$					(5)
	$\longrightarrow C_6H_5CH{:}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + C_2H_5OH$ (elim.) k'		B = 0.12			k'	30	3.92	-5		
	$\longrightarrow C_6H_5CH_2CH_2OC_2H_5 + p\text{-}CH_3C_6H_4SO_3^-$ (exchange) k''					k''	30	1.18	-4		
.9	$p\text{-}CH_3OC_6H_4CH_2CH_2OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.06;			$-dA/dt = (k' + k'')AB$					(5)
	$\longrightarrow p\text{-}CH_3OC_6H_4CH{:}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + C_2H_5OH$ (elim.) k'		B = 0.12			k'	30	1.69	-5		
	$\longrightarrow p\text{-}CH_3OC_6H_4CH_2CH_2OC_2H_5 + p\text{-}CH_3C_6H_4SO_3^-$ (exchange) k''					k''	30	8.61	-5		
.10	$p\text{-}ClC_6H_4CH_2CH_2OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.06;			$-dA/dt = (k' + k'')AB$					(5)
	$\longrightarrow p\text{-}ClC_6H_4CH{:}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + C_2H_5OH$ (elim.) k'		B = 0.12			k'	30	1.38	-4		
	$\longrightarrow p\text{-}ClC_6H_4CH_2CH_2OC_2H_5 + p\text{-}CH_3C_6H_4SO_3^-$ (exchange) k''					k''	30	2.93	-4		
.11	$m\text{-}BrC_6H_4CH_2CH_2OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.06;			$-dA/dt = (k' + k'')AB$					(5)
	$\longrightarrow m\text{-}BrC_6H_4CH{:}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + C_2H_5OH$ (elim.) k'		B = 0.12			k'	30	3.69	-4		
	$\longrightarrow m\text{-}BrC_6H_4CH_2CH_2OC_2H_5 + p\text{-}CH_3C_6H_4SO_3^-$ (exchange) k''					k''	30	5.53	-4		
	Sulfone-substituted Alkyl arylsulfonates										
.12	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH_3 + OH^- \longrightarrow$	DW 50*	10^3A = 4-5;	Na^+	= B	$k\,AB$	25	1.84	+2	*	(9) (10)
	$p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + H_2O$		10^3B = 4-5	KCl	0.1						

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.13	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH_3 + NH_3 \longrightarrow$	DW 50*	$10^2A = 1$;	M + N	.005-.015	k AB	25	7.10	-3	*	(11)
	$p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + NH_4^+$		$10^2B = 6\text{-}18$								
.14	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH + n\text{-}C_6H_{13}NH_2 \longrightarrow$	DW 50*	not stated			k AB	25	1.28	-1		(6)
	$p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + n\text{-}C_6H_{13}NH_3^+$	CH_3OH		M + N			25	8.17	-2		
		$CHCl_3$					25	9.17	-5		
		$CH_3COOC_2H_5$					25	3.58	-3		
		$CH_3C{:}N$					25	1.36	-2		
		Diox*					25	3.89	-3		
		C_6H_6					25	6.08	-4		
				M + N	0.003		25	2.44	-3		
				C_2H_5OH	0.5		25	2.24	-3		
		C_6H_5Cl					25	3.08	-4		
.15	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH_3 + (n\text{-}C_4H_9)_2NH \longrightarrow$	DW 50*	not stated			k AB	25	2.35	-1		(6)
	$p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + (n\text{-}C_4H_9)_2NH_2^+$	CH_3OH		M + N			25	7.19	-2		
		$CHCl_3$					25	9.17	-4		
		$CH_3COOC_2H_5$					25	3.25	-3		
		$CH_3C{:}N$					25	3.97	-2		
		Diox*					25	2.89	-3		
		C_6H_6					25	1.29	-3		
				M + N	0.0048		25	2.12	-3		
					0.0070		25	2.19	-3		
		C_6H_5Cl					25	1.26	-3		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.16	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH_3 + (CH_3)_3N \longrightarrow$ $p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + (CH_3)_3NH^+$	DW 50*	$10^2A = 1$; $10^2B = 5\text{-}9$	M + N	.003-.007	k AB	25	1.32	-1				*	(9) (11)
.17	$p\text{-}CH_3C_6H_4SO_2CH_2CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}CH_3 + (C_2H_5)_3N \longrightarrow$ $p\text{-}CH_3C_6H_4SO_2CH{:}CHCH_3 + p\text{-}CH_3C_6H_4SO_3^- + (C_2H_5)_3NH^+$	DW 50*	$10^2A = 1$; $10^2B = 6\text{-}10$	M + N	.005-.008	k AB	25	5.93	-2				*	(9) (11)
				$(C_2H_5)_3NH^+$ Cl^-			25	4.72	-2					(6)
		CH_3OH		M + N			25	9.31	-3					
		$CHCl_3$					25	1.46	-3					
		$CH_3COOC_2H_5$					25	7.69	-4					
		$CH_3C{:}N$					25	7.55	-3					
		Diox*					25	9.36	-4					
		C_6H_6					25	8.83	-4					
				C_2H_5OH	0.5		25	8.64	-4					
		C_6H_5Cl					25	1.76	-3					
.18	*threo*-$p\text{-}CH_3C_6H_4SO_2CH(CH_3)CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}Br + (CH_3)_3N \longrightarrow$  $+ p\text{-}BrC_6H_4SO_3^- + (CH_3)_3NH^+$	DW 50*	$10^4A = 2$; $10^2B = 2\text{-}6$			k AB	25	3.29	-3					(2)
							40	1.06	-2					
							50	2.20	-2	14.5	1.4	8		
.19	*erythro*-$p\text{-}CH_3C_6H_4SO_2CH(CH_3)CH(CH_3)OSO_2C_6H_4\text{-}p\text{-}Br + (CH_3)_3N \longrightarrow$  $+ p\text{-}BrC_6H_4SO_3^- + (CH_3)_3NH^+$	DW50*	$10^4A = 2$; $10^2B = 2\text{-}6$			k AB	25	7.62	-3					(2)
							40	2.17	-2					
							50	4.10	-2	12.8	2.0	7		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
	Sulfone-substituted Cyclo-alkyl arylsulfonates										
.20	*cis*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + OH^- ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + H_2O	DW 50*	10^3A = 4-5; 10^3B=4-5	KCl	0.1	*k* AB	25	4.34	+1		(9) (10)
.21	*cis*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(CH_3)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(CH_3)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 6-13	$LiNO_3$	.05-.15	*k* AB	25	1.56	-2	*	(9) (11)
.22	*cis*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(C_2H_5)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(C_2H_5)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 6-19			*k* AB	25	6.78	-3	*	(9) (11)
.23	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + OH^- ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + H_2O	DW 50* DW 70*	10^3A = 4-5; 10^3B = 4-5 A = B = 0.008	KCl	0.1	*k* AB	25 0	2.18 5.5	0 -1		(9) (10) (1)
.24	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(CH_3)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(CH_3)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 6-20			*k* AB	25	1.30	-2	*	(9) (11)
.25	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CHCH_2CH_2CH_2}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(C_2H_5)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CHCH_2CH_2}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(C_2H_5)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 6-19			*k* AB	25	1.01	-3	*	(9) (11)
.26	*cis*-*p*-$CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4$-*p*-$CH_3$ + OH^- ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + H_2O	DW 50*	10^3A = 4-5; 10^3B = 4-5	KCl	0.1	*k* AB	25	1.51	+1		(9) (10)

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.27	$cis\text{-}p\text{-}CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4\text{-}p\text{-}CH_3 + (CH_3)_3N \longrightarrow$ $p\text{-}CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + (CH_3)_3NH^+$	DW 50*	$10^2A = 1$; $10^2B = 6\text{-}20$			k AB	25	2.87	-3				*	(9) (11)
.28	$cis\text{-}p\text{-}CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4\text{-}p\text{-}CH_3 + (C_2H_5)_3N \longrightarrow$ $p\text{-}CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + (C_2H_5)_3NH^+$	DW 50*	$10^2A = 1$; $10^2B = 6\text{-}19$			k AB	25	9.3	-4				*	(9) (11)
.29	$trans\text{-}p\text{-}CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4\text{-}p\text{-}CH_3 + OH^- \longrightarrow$ $p\text{-}CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2 + p\text{-}CH_3C_6H_4SO_3^- + H_2O$	DW 50*	$10^3A = 4\text{-}5$; $10^3B = 4\text{-}5$	KCl	0.1	k AB	25	3.50	-2					(9) (10)
		DW 55*	$10^3A = 6\text{-}17$; $10^3B = 6\text{-}33$				20	2.24	-2					(1)
							30	5.77	-2					
							40	1.51	-1	17.4	2.2	11		
		DW 60*	$10^3A = 6\text{-}17$; $10^3B = 6\text{-}33$				12	1.07	-2					
							20	2.56	-2					
							30	6.70	-2					
							40	1.78	-1	17.6	3.4	11		
		DW 70*	$10^3A = 6\text{-}17$; $10^3B = 6\text{-}33$				0	4.25	-3					
							10	1.34	-2					
							20	3.90	-2					
							30	9.94	-2					
							40	2.61	-1	17.4	3.9	11		
		DW 77.5*	$10^3A = 6\text{-}17$; $10^3B = 6\text{-}33$				10	2.47	-2					
							20	7.06	-2					
							30	1.89	-1					
							40	4.78	-1	17.4	7	11		
		DW 85*	$10^3A = 6\text{-}17$; $10^3B = 6\text{-}33$				12	5.66	-2					
							20	1.44	-1					
							30	4.21	-1	19	2	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.30	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(CH_3)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(CH_3)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 8-25			*k* AB	25	1.2	-4				*	(9) (11)
.31	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(C_2H_5)_3N$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(C_2H_5)_3NH^+$	DW 50*	10^2A = 1; 10^2B = 6-19			*k* AB	25	8.0	-6				*	(9) (11)
.32	*trans*-*p*-$CH_3C_6H_4SO_2\overline{CH(CH_2)_4}CHOSO_2C_6H_4$-*p*-$CH_3$ + $(CH_2)_5NH$ ⟶ *p*-$CH_3C_6H_4SO_2\overline{C{:}CH(CH_2)_3}CH_2$ + *p*-$CH_3C_6H_4SO_3^-$ + $(CH_2)_5NH_2^+$	DW 50*	10^2A = 1; 10^2B = 6-18			*k* AB	25	5.1	-4				*	(11)

CODED SOLVENTS

Ac*	0.02 M $(CH_3CO)_2O$ in CH_3COOH
Diox*	Dioxane
DW 50*(55) (60) (70) (77.5) (85)	Volume % Dioxane indicated + H_2O

COMMENTS

General. Reactants are listed in the order of increasing complexity of the alkyl group. Primary precede secondary precede tertiary except that cyclo follow tertiary. Aryl substituted alkyl follow cyclo and sulfonyl substituted alkyl follow aryl-substituted. Parallel ester exchange to varying extent occurs in acid solvents. See 222.461. Parallel solvolysis occurs in aqueous and alcoholic solvents. See 212.461.

Reaction. **(.1)** Rate constant for elimination reaction only, which accounts for about one third of total reaction. Olefin distribution is 10.3% $CH_2{:}CHCH_2CH_3$; 89.7% $CH_3CH{:}CHCH_3$ with 43.2% cis and 46.5% trans-isomer. **(.2)** Extent of parallel ester exchange not determined. Rate constant is for total reaction, elimination and solvolysis. **(.3)** Products determined were 50% ester exchange and 31.5% olefin made up of 15.7% $CH_2{:}CHC_3H_7$, 35% *cis*-$CH_3CH{:}CHC_2H_5$ and 49% *trans*-$CH_3CH{:}CHC_2H_5$. **(.4)** Products determined were 36% ester exchange and 46% olefin made up of 20% $(CH_3)_2CHCH_2CH{:}CH_2$, 27% *cis*-$(CH_3)_2CHCH{:}CHCH_3$ and 53% *trans*-$(CH_3)_2CHCH{:}CHCH_3$. **(.5)** Products determined were 12% ester exchange and 68% olefin made up of 24% $(CH_3)_3CCH_2CH{:}CH_2$, 1% *cis*-$(CH_3)_3CCH{:}CHCH_3$ and 75% *trans*-$(CH_3)_3CCH{:}CHCH_3$. **(.6)** Elimination accounts for only 39% of reaction with ester exchange accounting for 61%, see 222.461. **(.7)** Elimination accounts for 85% and ester exchange for only 15% of reaction. **(.12)** Extent of any parallel solvolysis reaction not indicated. **(.13) (.16) (.17)** Rate constant corrected for simultaneous (.12), elimination catalyzed by OH^-. **(.21) (.22)** Rate constant corrected for simultaneous (.20) elimination catalyzed by OH^-. **(.24) (.25)** Rate constant corrected for simultaneous (.23) elimination catalyzed by OH^-. **(.27) (.28)** Rate constant corrected for simultaneous (.26) elimination catalyzed by OH^-. **(.30) (.31) (.32)** Rate constant corrected for simultaneous (.29) elimination catalyzed by OH^-.

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LITERATURE

(1) F.G. Bordwell, R.J. Kern, *ACS* 1955, **77**, 1141. (2) F.G. Bordwell, P.S. Landis, *ACS* 1957, **79**, 1593. (3) F.G. Bordwell, M.L. Peterson, *ACS* 1955, **77**, 1145. (4) H.C. Brown, M. Nakagawa, *ACS* 1955, **77**, 3614. (5) C.H. DePuy, D.H. Froemsdorf, *ACS* 1957, **79**, 3710. (6) R.G. Pearson, D.C. Vogelsong, *ACS* 1958, **80**, 1048. (7) J.D. Roberts, W. Bennett, R.E. McMahon, E.W. Holroyd, *ACS* 1952, **74**, 4283. (8) J.D. Roberts, V.C. Chambers, *ACS* 1951, **73**, 5034. (9) J. Weinstock, R.G. Pearson, F.G. Bordwell, *ACS* 1954, **76**, 4748. (10) J. Weinstock, R.G. Pearson, F.G. Bordwell, *ACS* 1956, **78**, 3468. (11) J. Weinstock, R.G. Pearson, F.G. Bordwell, *ACS* 1956, **78**, 3473.

ELIMINATION

Bond Unsaturation

Elimination of $ArSO_3^-$ and halide ion to form C:C

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $>C(X)-C(OSO_2Ar)< + 3I^- \longrightarrow >C=C< + ArSO_3^- + X^- + I_3^-$

Rate measured: $+dO/dt$

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	*cis*-$CH_2(CH_2)_3CHBrCHOSO_2C_6H_4$-*p*-$CH_3$ + $3I^-$ ⟶ *cyclo*-C_6H_{10} + Br^- + *p*-$CH_3C_6H_4SO_3^-$ + I_3^-	*n*-C_3H_7OH	10^2A = 1.5-2.2; B = 0.15-0.3	*k* AB	62	6.19	-7			
					88	7.50	-6	23	6	8
.2	*trans*-$CH_2(CH_2)_3CHBrCHOSO_2C_6H_4$-*p*-$CH_3$ + $3I^-$ ⟶ *cyclo*-C_6H_{10} + Br^- + *p*-$CH_3C_6H_4SO_3^-$ + I_3^-	*n*-C_3H_7OH	10^2A = 2-18; B = 0.2-0.4	*k* AB	48.8	7.73	-6			
					62.4	3.80	-5			
					74.2	1.22	-4	24.0	1.6	11
.3	*cis*-$CH_2(CH_2)_3CHBrCHOSO_2C_6H_4$-*p*-Br + $3I^-$ ⟶ *cyclo*-C_6H_{10} + Br^- + *p*-$BrC_6H_4SO_3^-$ + I_3^-	*n*-C_3H_7OH	10^2A = 1.4-3; B = 0.15-0.3	*k* AB	62.4	3.03	-6			
					74.2	1.07	-5			
					88.2	3.77	-5	23.5	3	10
.4	*trans*-$CH_2(CH_2)_3CHBrCHOSO_2C_6H_4$-*p*-Br + $3I^-$ ⟶ *cyclo*-C_6H_{10} + Br^- + *p*-$BrC_6H_4SO_3^-$ + I_3^-	*n*-C_3H_7OH	10^2A = 1.5-2.4; B = 0.15-0.5	*k* AB	49	3.38	-5			
					62	1.56	-4			
					74	4.72	-4	23	1.2	11

COMMENTS

Calculated second order rate constants decreased with progress of reaction but were constant with variation of initial concentrations of both A and B. Rate constants tabulated are for initial 20% reaction.

LITERATURE

S.J. Cristol, J.Q. Weber, M.C. Brindell, *ACS* 1956, **78**, 598.

ELIMINATION
of Hydrogen halide
Double Bond formation

Liquid phase

Reaction type:

$$\underset{(A)}{>CX\text{-}CH<} + \underset{(B)}{B} \longrightarrow \underset{(L)}{>C{:}C<} + \underset{(M)}{BH^+} + \underset{(N)}{X^-}$$

$$>CX\text{-}CH< + B^- \longrightarrow >C{:}C< + BH + X^-$$

Rate measured = dL/dt

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents at the end of the table.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.52		$n\text{-}C_3H_7Br + C_2H_5O^- \longrightarrow$ $CH_3CH{:}CH_2 + C_2H_5OH + Br^-$	C_2H_5OH	A = B = 0.1	Na^+	= B	k AB	55	5.3	-5				*	(32)
.53		$(CH_3)_2CHBr + H_2O \longrightarrow CH_3CH{:}CH_2 + H_3O^+ + Br^-$	Et 60*	A = 0.1-0.15			k A	80	3.2	-6				*	(30)
.54	.10	$(CH_3)_2CHBr + OH^- \longrightarrow CH_3CH{:}CH_2 + H_2O + Br^-$	C_2H_5OH	A = 0.1-0.2; B = 4	K^+	= B	k AB	80	1.41	-3				*	(30)
.55	.9	$(CH_3)_2CHBr + C_2H_5O^- \longrightarrow$ $CH_3CH{:}CH_2 + C_2H_5OH + Br^-$	C_2H_5OH•	A = 0.05-.2; B = 1.0	Na^+	= B	k AB	25	1.89	-6				* (30) (51)	(54)
								35	7.17	-6					(54)
								45	2.66	-5					
								55	8.49	-5	24.8	3	12		
.56		$(CH_3)_2CDBr + C_2H_5O^- \longrightarrow$ $CH_3CD{:}CH_2 + C_2H_5OH + Br^-$	C_2H_5OH	A = 0.05; B = 1.0	Na^+	= B	k AB	25	1.68	-6				*	(51)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.57		$(CD_3)_2CHBr + C_2H_5O^- \longrightarrow CD_3CH{:}CD_2 + C_2H_5OD + Br^-$	C_2H_5OH	A = 0.05; B = 1.0	Na^+	= B	k AB	25	2.9	-7				*	(51)
.58		$n\text{-}C_4H_9Br + C_2H_5O^- \longrightarrow C_4H_8 + C_2H_5OH + Br^-$	C_2H_5OH	A = B = 0.1	Na^+	= B	k AB	55	4.3	-5				*	(32)
.59		$n\text{-}C_4H_9I + HC{:}ONH_2 \longrightarrow C_4H_8$, HCOOH, R_4N^+, I^-	$HC{:}ONH_2$	A = 0.1			k A	25	3.39	-7				*	(41)
.60		$(CH_3)_2CHCH_2Br + C_2H_5O^- \longrightarrow (CH_3)_2C{:}CH_2 + C_2H_5OH + Br^-$	C_2H_5OH	A = B = 0.1	Na^+	= B	k AB	55	8.5	-5				*	(32)
.61		$C_2H_5(CH_3)CHF + C_2H_5O^- \longrightarrow C_4H_8 + C_2H_5OH + F^-$	C_2H_5OH	A = 0.8; B = 1			k AB	120	6.7	-7				*	(10a)
.62		$C_2H_5(CH_3)CHBr + H_2O \longrightarrow C_4H_8 + H_3O^+ + Br^-$	Et 60*	A = 0.1-0.15			k A	80	6.3	-6				*	(30)
.63		$C_2H_5(CH_3)CHBr + OH^- \longrightarrow C_4H_8 + H_2O + Br^-$	C_2H_5OH	A = 0.1-0.2; B = 4	K^+	= B	k AB	80	1.91	-3				*	(30)
.64		$C_2H_5(CH_3)CHBr + C_2H_5O^- \longrightarrow C_4H_8 + C_2H_5OH + Br^-$	C_2H_5OH	A = 0.2; B = 1	Na^+	= B	k AB	25	3.47	-6				*	(30)
.65		$C_2H_5(CH_3)CHI + HC{:}ONH_2 \longrightarrow C_4H_8$, HCOOH, R_4N^+, I^-	$HC{:}ONH_2$	A = 0.1			k A	25	7.22	-7				*	(41)
.66		$(CH_3)_3CF + C_2H_5O^- \longrightarrow (CH_3)_2C{:}CH_2 + C_2H_5OH + F^-$	C_2H_5OH	A = 0.8; B = 1			k AB	118 138	1.39 6.6	-6 -6	 24.8	 1.0	 8	*	(10a)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.67		$(CH_3)_3CCl + C_2H_5O^- \longrightarrow$ $(CH_3)_2C{:}CH_2, (CH_3)_3COC_2H_5, C_2H_5OH, Cl^-$	C_2H_5OH	A = 0.2; B = 0.54	Na^+	= B	k AB	44	4.3	-6				*	(28)
.68		$(CH_3)_3CCl + C_6H_5S^- \longrightarrow$ $(CH_3)_2C{:}CH_2 + C_6H_5SH + Cl^-$	C_2H_5OH	A = 0.3; B = 0.2	Na^+	= B	k AB	45	4.83	-5				*	(28)
				0.7				45	4.10	-5					
								58	2.02	-4					
								68	6.02	-4	24.8	4	12		
.69		$(CH_3)_3CCl + (CH_3)_2NCHO \longrightarrow$	B	10^2A = 6-9			k A	51	9.5	-8				*	(49)
								80	2.44	-6	25	8	9		
.70	.14	$(CH_3)_3CBr + C_2H_5O^- \longrightarrow$ $(CH_3)_2C{:}CH_2 + C_2H_5OH + Br^-$	C_2H_5OH	A = 0.1 ; B = 0	Na^+	= B	k A	25	8.6	-7				*	(31)
				0.017 0.024				25	1.35	-6					
				0.064 0.083				25	2.94	-6					
				0.038 1.0				25	3.00	-5					
.71		$(CH_3)_3CBr \longrightarrow (CH_3)_2C{:}CH_2 + H^+ + Br^-$	CH_3NO_2	A = 0.02	$(C_2H_5)_4NCl$	0.005	k A	25	4.0	-6				*	(27)
						0.011		25	4.5	-6					
						0.020		25	5.3	-6					
						0.051		25	7.4	-6					
						0.073		25	8.9	-6					
						0.098		25	1.10	-5					
						0.141		25	1.43	-5					
.72		$(CH_3)_3CBr + HC{:}ONH_2 \longrightarrow (CH_3)_2C{:}CH_2$	$HC{:}ONH_2$	A = 0.1			k A	25	2.4	-6				*	(41)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.73	$(CH_3)_3CBr + HC{:}ON(CH_3)_2 \longrightarrow (CH_3)_2C{:}CH_2$	B	$10^2A = 8.4$			kA	25	2.6	-6				*	(49)
			16				40	1.5	-5					
			0.9				51	4.3	-5	22.1	3	10		
			8.6	$(C_2H_5)_4NNO_3$	0-.008		51	5.2	-5					
			8.4		0.042		51	5.7	-5					
			8.3		0.097		51	7.0	-5					
			8.5		0.167		51	8.0	-5					
			8.6	$(C_2H_5)_4NBr$	0.076		51	7.7	-5					
			8.3	NaBr	0.104		51	8.7	-5					
.74	$(CH_3)_3CBr + C_2H_5C{:}ONHCH_3 \longrightarrow (CH_3)_2C{:}CH_2$	B	$10^2A = 1.4$			kA	25	2.3	-6				*	(49)
			10-20				39	1.25	-5					
			8				51	5.0	-5	23				
			8	$(C_2H_5)_4NNO_3$	0.10		51	5.4	-5					
			8	NaBr	0.09		51	4.9	-5					
.75	$(CH_3)_3CBr + C_5H_5N \longrightarrow (CH_3)_2C{:}CH_2 + C_5H_5NH^+ + Br^-$	SO_2	$10^2A = 3\text{-}5;\ 10^2B = 9.1$	$-(dA/dt)_{t=o} =$		k_oA	-15	1.75	-4				*	(10)
			17				-15	2.00	-4					
			41				-15	2.20	-4					
.76	$n\text{-}C_5H_{11}F + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + F^-$	C_2H_5OH	$A = 0.4\text{-}0.9;\ B = 0.5\text{-}1$			kAB	80	1	-8				*	(10a)
.77	$n\text{-}C_5H_{11}Br + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + Br^-$	C_2H_5OH	$A = B = 0.1$	Na^+	$= B$	kAB	55	3.5	-5				*	(32)
.78	$(CH_3)_2CHCH_2CH_2F + C_2H_5O^- \longrightarrow$ $(CH_3)_2CHCH{:}CH_2 + C_2H_5OH + F^-$	C_2H_5OH	$A = 0.8;\ B = 1$			kAB	119	5	-7				*	(10a)

Supplement 1958

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.79		$C_2H_5CH(CH_3)CH_2F + C_2H_5O^- \longrightarrow C_2H_5(CH_3)C{:}CH_2 + C_2H_5OH + F^-$	C_2H_5OH	A = 0.8; B = 1			k AB	121	4	-7				*	(10a)
.80		$(CH_3)_3CCH_2Br + Ag^+ \longrightarrow (CH_3)_2(C_2H_5)COH,\ (CH_3)_2C{:}CHCH_3,\ AgBr$	Et 70*	A = 0.1; B = 0.14	NO_3^-	= B	k AB	92 109	1.13 4.25	-3 -3	 22.5	 3	 10	*	(1)
.81		$C_3H_7(CH_3)CHF + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + F^-$	C_2H_5OH	A = 0.8; B = 1			k AB	139 162	3.0 1.1	-6 -5	 20	 1	 6	*	(10a)
.82		$C_3H_7(CH_3)CHBr + H_2O \longrightarrow C_5H_{10} + H_3O^+ + Br^-$	Et 60*	A = 0.1-0.15			k A	80	3.8	-6				*	(30)
.83		$C_3H_7(CH_3)CHBr + OH^- \longrightarrow C_5H_{10} + H_2O + Br^-$	C_2H_5OH	A = 0.1-0.2; B = 4.0	K^+	= B	k AB	80	1.49	-3				*	(30)
.84		$C_3H_7(CH_3)CHBr + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + Br^-$	C_2H_5OH	A = 0.2; B = 1.0	Na^+	= B	k AB	25	2.77	-6				*	(30)
.85		$(C_2H_5)_2CHBr + H_2O \longrightarrow C_5H_{10} + H_3O^+ + Br^-$	Et 60*	A = 0.1-0.15			k A	80	9.0	-6				*	(30)
.86		$(C_2H_5)_2CHBr + OH^- \longrightarrow C_5H_{10} + H_2O + Br^-$	C_2H_5OH	A = 0.1-0.2; B = 4.0	K^+	= B	k AB	80	2.04	-3				*	(30)
.87		$(C_2H_5)_2CHBr + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + Br^-$	C_2H_5OH	A = 0.2; B = 1.0	Na^+	= B	k AB	25	4.00	-6				*	(30)
.88		$C_2H_5(CH_3)_2CF + C_2H_5O^- \longrightarrow C_5H_{10} + C_2H_5OH + F^-$	C_2H_5OH	A = 1.15; B = 1.0			k AB	120 140	1.21 5.2	-6 -6	 23.5	 1.4	 7	*	(10a)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.89	.17	$C_2H_5(CH_3)_2CCl + H_2O \longrightarrow$ $C_5H_{10} + H_3O^+ + Cl^-$	Et 80*	A = 0.05			k A	25	5.2	-6				*	(3) (4) (40) (52) (53)
			BC 85*					25	2.86	-6				*	(7)
.90		$CH_3CD_2(CH_3)_2CCl + H_2O \longrightarrow$ $C_5H_9D,\ C_5H_8D_2,\ H_3O^+,\ DH_2O^+,\ Cl^-$	Et 80*	A = 0.04			k A	25	2.7	-6				*	(52)
.91		$C_2H_5(CD_3)_2CCl + H_2O \longrightarrow$ $C_5H_4D_6,\ C_5H_5D_5,\ H_3O^+,\ DH_2O^+,\ Cl^-$	Et 80*	A = 0.04			k A	25	3.3	-6				*	(52)
.92		$CH_3CD_2(CD_3)_2CCl + H_2O \longrightarrow$ $C_5H_3D_7 + DH_2O^+ + Cl^-$	Et 80*	A = 0.04			k A	25	1.5	-6				*	(52)
.93		$C_2H_5(CH_3)_2CBr + H_2O \longrightarrow$ $\longrightarrow C_5H_{10} + H_3O^+ + Br^-$ (E) $\longrightarrow C_2H_5(CH_3)_2COH + HBr$ (S)	BC 85*			k A = $(k_E + k_S)$ A		25	k=1.07	-4				*	(7) (8)
								25	k_E=2.9	-5					
								25	k_S=7.8	-5					
.94		$C_2H_5(CH_3)_2CBr + C_2H_5O^- \longrightarrow$ $C_5H_{10} + C_2H_5OH + Br^-$	C_2H_5OH	10^2A = 7.3; 10^2B = 0	Na^+	= B	k A	25	4.3	-6				*	(31)
				1.6 2.3				25	5.4	-6					
				6.4 8.5				25	8.8	-6					
				3.9 102				25	6.12	-5					
				3.4 201				25	7.02	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.95	$(CH_3)_2CHCH_2(CH_3)CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	B = 1.0	Na^+	= B	k AB;	25	k = 1.69	-6				*	(54)
	$\longrightarrow C_6H_{12} + C_2H_5OH + Br^-$ (E)					$k = k_E + k_S$	25	k_E = 1.42	-6					
	$\longrightarrow (CH_3)_2CHCH_2(CH_3)CHOH + HBr$ (S)						25	k_S = 2.7	-7					
.96	$(n\text{-}C_3H_7)(CH_3)_2CCl + H_2O \longrightarrow C_6H_{12} + H_3O^+ + Cl^-$	Et 80*	A = 0.06			k A	25	4.8	-6				*	(3) (4)
.97	$(n\text{-}C_3H_7)(CH_3)_2CBr + H_2O \longrightarrow$	BC 85*				k A;	25	k = 8.25	-5				*	(8)
	$\longrightarrow C_6H_{12} + H_3O^+ + Br^-$ (E)					$k = k_E + k_S$	25	k_E = 2.6	-5					
	$\longrightarrow (n\text{-}C_3H_7)(CH_3)_2COH + HBr$ (S)						25	k_S = 5.6	-5					
.98	$(CH_3)_2CH(CH_3)_2CCl + H_2O \longrightarrow C_6H_{12} + H_3O^+ + Cl^-$	Et 80*	A = 0.05			k A	25	6.0	-6				* (3) (4) (53) (57)	
							36	2.45	-5					
							45	7.0	-5					
							55	2.1	-4	23	5	11		
.99	$(CH_3)_2CD(CH_3)_2CCl + H_2O \longrightarrow$	Et 80*	A = 0.05			k A	25	4.26	-6				*	(53)
	C_6H_{12}, $C_6H_{11}D$, H_3O^+, DH_2O^+, Cl^-						36	1.82	-5					
							45	5.45	-5					
							55	1.66	-4					
.100	$(CH_3)_2CH(CH_3)_2CBr + H_2O \longrightarrow$	BC 85*				k A;	25	k = 5.47	-5				*	(7)
	$\longrightarrow C_6H_{12} + H_3O^+ + Br^-$ (E)					$k = k_E + k_S$	25	k_E = 3.2	-5					
	$\longrightarrow (CH_3)_2CH(CH_3)_2COH + HBr$ (S)						25	k_S = 2.3	-5					
.101	$CH_3(C_2H_5)_2CCl + H_2O \longrightarrow C_6H_{12} + H_3O^+ + Cl^-$	Et 80*	A = 0.05			k A	25	1.00	-5				* (2) (3) (4) (47)	

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.102	$CH_3(C_2H_5)_2CBr + H_2O \longrightarrow C_6H_{12} + H_3O^+ + Br^-$ (E)	BC 85*				k A;	25	k = 1.14	-4				*	(7)
	$\longrightarrow CH_3(C_2H_5)_2COH + HBr$ (S)					$k = k_E + k_S$	25	k_E = 4.6	-5					
							25	k_S = 6.5	-5					
.103	$(CH_3)_3CCH_2(CH_3)CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	B = 1.0	Na^+	= B	k AB;	35	k = 4.72	-6				*	(54)
	$\longrightarrow C_7H_{14} + C_2H_5OH + Br^-$ (E)					$k = k_E + k_S$	45	k = 1.58	-5					
	$\longrightarrow (CH_3)_3CCH_2(CH_3)CHOC_2H_5 + Br^-$ (S)						55	k = 4.76	-5					
							35	k_E = 4.11	-6					
							45	k_E = 1.41	-5					
							55	k_E = 4.19	-5	23.2	1.2	11		
							35	k_S = 6.1	-7					
							45	k_S = 1.7	-6					
							55	k_S = 5.7	-6	23.2	1.7	10		
.104	$(n\text{-}C_4H_9)(CH_3)_2CCl + H_2O \longrightarrow C_7H_{14} + H_3O^+ + Cl^-$	Et 80*				k A	25	4.5	-6				*	(2) (3) (4)
.105	$(CH_3)_2CHCH_2(CH_3)_2CBr + H_2O \longrightarrow$	BC 85*				k A;	25	k = 1.94	-4				*	(8)
	$\longrightarrow C_7H_{14} + H_3O^+ + Br^-$ (E)					$k = k_E + k_S$	25	k_E = 8.9	-5					
	$\longrightarrow (CH_3)_2CHCH_2(CH_3)_2COH + HBr$ (S)						25	k_S = 1.0	-4					
.106	$(CH_3)_3C(CH_3)_2Cl + H_2O \longrightarrow (CH_3)_3C(CH_3)C{:}CH_2 + H_3O^+ + Cl^-$	Et 80*	A = 0.06			k A	25	6.8	-6				*	(3) (4) (57)
.107	$(CH_3)_3C(CH_3)_2CCl + (CH_3)_2NCHO \longrightarrow$	B	10^2A = 1-8			k A	25	1.4	-7				*	(49)
.108	$(CH_3)_3C(CH_3)_2CCl + C_2H_5C{:}ONHCH_3 \longrightarrow$	B	10^2A = 1-8			k A	25	4.4	-7				*	(49)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.109	$(C_2H_5)_3CCl + H_2O \longrightarrow (C_2H_5)_2C{:}CHCH_3 + H_3O^+ + Cl^-$	Et 80*	A = 0.06	k A	25	1.10	-5				*	(3) (4)
.110	$(CH_3)_3CCH_2(CH_3)_2CCl + H_2O \longrightarrow C_8H_{16} + H_3O^+ + Cl^-$	Et 80*		k A	0	3.9	-6				*	(2)
					15	3.4	-5					
					25	1.29	-4	22.9	1	13	(2) (4) (40)	
		BC 85*			25	1.19	-5					(7)
.111	$(CH_3)_3CCH_2(CH_3)_2CBr + H_2O \longrightarrow C_8H_{16} + H_3O^+ + Br^-$ (E) $\searrow (CH_3)_3CCH_2(CH_3)_2COH + HBr$ (S)	BC 85*		k A; $k = k_E + k_S$	25	$k = 1.31$	-3				*	(7) (8)
					25	$k_E = 7.5$	-4					
					25	$k_S = 5.6$	-4					
.112	$C_2H_5(CH_3)_2C(CH_3)_2CCl + H_2O \longrightarrow C_8H_{16} + H_3O^+ + Cl^-$	Et 80*		k A	25	2.9	-5				*	(9)
.113	$(CH_3)_2CH(C_2H_5)_2CCl + H_2O \longrightarrow C_8H_{16} + H_3O^+ + Cl^-$	Et 80*	A = 0.06	k A	25	1.4	-5				*	(3) (4)
.114	$CH_3[(CH_3)_2CH]_2CCl + H_2O \longrightarrow C_8H_{16} + H_3O^+ + Cl^-$	Et 80*		k A	25	1.05	-4				*	(4) (5)
.115	$(CH_3)_3C(C_2H_5)_2CCl + H_2O \longrightarrow C_9H_{18} + H_3O^+ + Cl^-$ (α-isomer)	Et 80*	A = 0.06	k A	25	4.0	-4				*	(3) (4)
.116	$(CH_3)_3C(C_2H_5)_2CCl + H_2O \longrightarrow C_9H_{18} + H_3O^+ + Cl^-$ (β-isomer)	Et 80*	A = 0.06	k A	25	1.0	-4				*	(3) (4)
.117	$[(CH_3)_3CCH_2]_2(CH_3)CCl \longrightarrow C_{12}H_{24} + HCl$	A		k A	25	5	-6				*	(2)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.118	$[(CH_3)_3CCH_2]_2(CH_3)CCl + H_2O \longrightarrow C_{12}H_{24} + H_3O^+ + Cl^-$	Et 80*		k A	0	2.51	-4				*	(2)
					15	1.61	-3					
					25	5.25	-3	19.6	1.2	12		
		Et 90*			0	6.84	-5					
					15	4.59	-4					
					25	1.52	-3	20.2	1.0	12		
		Et 95*			0	2.62	-5					
					15	1.95	-4					
					25	6.65	-4	21.0	1.6	12		
.119	$[(CH_3)_2CCH_2]_2(CH_3)CCl + C_2H_5OH \longrightarrow C_{12}H_{24} + C_2H_5OH_2^+ + Cl^-$	C_2H_5OH		k A	15	6.34	-5				*	(2)
					25	2.24	-4					
					35	7.40	-4	21.6	1.5	12		
	Cyclo-alkyl halides											
.120	$cyclo\text{-}C_3H_5Cl + \left.\begin{matrix}H_2O\\C_2H_5OH\end{matrix}\right\} \longrightarrow$	Et 50*	A = 0.5-1	k A; $k = k_E + k_S$	95	1	-7				*	(48)
					200	1.3	-5					
.121	$cyclo\text{-}C_4H_7Cl + \left.\begin{matrix}H_2O\\C_2H_5OH\end{matrix}\right\} \longrightarrow$	Et 50*	A = 0.5-1	k A; $k = k_E + k_S$	95	3.8	-4				*	(48)
.122	$cyclo\text{-}C_5H_9Cl + \left.\begin{matrix}H_2O\\C_2H_5OH\end{matrix}\right\} \longrightarrow cyclo\text{-}C_5H_8 + H_3O^+ + Cl^-$ (E)	Et 50*	A = 0.5-1	k A; $k = k_E + k_S$	95	$k = 1.33$	-4					(48)
	$\searrow C_5H_9OH,\ C_5H_9OC_2H_5 + HCl$ (S)				95	$k_E = 4.8$	-5					
					95	$k_S = 8.5$	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.123	*cyclo*-$C_6H_{11}F + C_2H_5O^- \longrightarrow$ *cyclo*-$C_6H_{10} + C_2H_5OH + F^-$	C_2H_5OH	A = 0.9; B = 1.1			k AB	139 161	1.76 8.0	-6 -6				*	(10a)
.124	*cyclo*-$C_6H_{11}Cl$ + H_2O, C_2H_5OH $\longrightarrow$	Et 50*	A = 0.5-1			k A; $k = k_E + k_S$	95	9.2	-6				*	(48)
.125	*cyclo*-$C_6H_{11}Cl + OH^- \longrightarrow$ *cyclo*-$C_6H_{10} + H_2O + Cl^-$	Et 80*	10^2A = 1.5-3; B = 0.11		$-dB/dt = k$ AB		80 100	3.11 2.22	-5 -4	25.6	2	11	*	(33)
.126	*cyclo*-$C_6H_{11}Br$ + H_2O, C_2H_5OH $\longrightarrow$	Et 80*	10^2A = 2-5			k A; $k = k_E + k_S$	80 100	3.45 2.31	-6 -5	25.0	1.1	10	*	(33)
.127	*cyclo*-$C_6H_{11}Br + OH^- \longrightarrow$ *cyclo*-$C_6H_{10} + H_2O + Br^-$	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB	49.8 79.8	8.42 1.70	-5 -3	22.7	2	11	* $\Delta S^{\ddagger}$ = 22.0	(33)
.128	*cyclo*-$C_6H_{11}Br + Cl^- \longrightarrow$ *cyclo*-$C_6H_{10} + H^+ + Cl^- + Br^-$	An 90*	A = B = 0.07			k AB	69	2.3	-6				*	(55)
.129	*cyclo*-1-$CH_3C_5H_8Cl + H_2O \longrightarrow C_6H_{10} + H_3O^+ + Cl^-$ (E) $\searrow$ 1-$CH_3C_5H_8OH + HCl$ (S)	Et 80*				k A; $k = k_E + k_S$	25 25 25	k = 3.84 k_E = 1.88 k_S = 1.96	-4 -4 -4					(6)
.130	*cyclo*-1-$CH_3C_6H_{10}Cl + H_2O \longrightarrow C_7H_{12} + H_3O^+ + Cl^-$ (E) $\searrow$ 1-$CH_3C_6H_{10}OH + HCl$ (S)	Et 80*				k A; $k = k_E + k_S$	25 25 25	k = 3.17 k_E = 2.28 k_S = 8.9	-6 -6 -7					(6)
.131	*cyclo*-1-$CH_3C_7H_{12}Cl + H_2O \longrightarrow C_8H_{14} + H_3O^+ + Cl^-$ (E) $\searrow$ 1-$CH_3C_7H_{12}OH + HCl$ (S)	Et 80*				k A; $k = k_E + k_S$	25 25 25	k = 2.92 k_E = 1.38 k_S = 1.54	-4 -4 -4					(6)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.132	*cyclo*-1,2-$(CH_3)_2C_6H_9Cl + H_2O \longrightarrow C_8H_{14} + H_3O^+ + Cl^-$ (E) $\searrow$ 1,2-$(CH_3)_2C_6H_9OH + HCl$ (S)	Et 80*				kA; $k = k_E + k_S$	25	k=4.67	-6	*	(6)
.133	*cyclo-cis*-1,2-$(CH_3)_2C_6H_9Br + OH^- \longrightarrow C_8H_{14} + H_2O + Br^-$	Et 98*	$10^2A \simeq 1$; B = 0 0.345 0.52	Na^+	= B	kA	25 25 25	6.0 1.63 2.43	-6 -5 -5	*	(44)
.134	*cyclo-trans*-1,2-$(CH_3)_2C_6H_9Br + OH^- \longrightarrow C_8H_{14} + H_2O + Br^-$	Et 98*	$10^2A \simeq 2$; 10^2B = 0 3.95 7.90 34.5 52.0	Na^+	= B	kA	25 25 25 25 25	6.0 2.0 2.7 8.7 1.47	-6 -5 -5 -5 -4	*	(44)
.135	*cyclo-trans*-1,2-$(CH_3)_2C_6H_9Br + CH_3O^- \longrightarrow C_8H_{14} + CH_3OH + Br^-$	CH_3OH	$10^2A \simeq 2$; 10^2B = 0 1.51 3.03 6.05 1.58	Na^+	= B	kA	25 25 25 25 25	6.0 7.0 7.7 9.0 1.11	-5 -5 -5 -5 -4	*	(44)
.136	*cyclo*-1,4-$(CH_3)_2C_6H_9Cl + H_2O \longrightarrow C_8H_{14} + H_3O^+ + Cl^-$	Et 80*				kA	25	2.72	-6	*	(6)
.137	*cyclo*-1,4-$(CH_3)_2C_7H_{11}Cl + H_2O \longrightarrow C_9H_{16} + H_3O^+ + Cl^-$	Et 80*				kA	25	2.97	-6	*	(6)
.138	*cyclo*-5-CH_3-2-$(CH_3)_2CHC_6H_9Cl + H_2O \longrightarrow C_{10}H_{18} + H_3O^+ + Cl^-$ (menthyl chloride)	Et 80* C_2H_5OH	A = 0.12			kA	125 160	2 6.8	-6 -6	*	(39a)
.139	(+)$C_{10}H_{19}Cl + H_2O \longrightarrow C_{10}H_{18} + H_3O^+ + Cl^-$ (neomenthyl chloride)	Et 80*	10^2A = 9			kA	125	1.57	-4	*	(39a)

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.140	$(+)C_{10}H_{19}Cl + C_2H_5O^- \longrightarrow C_{10}H_{18} + C_2H_5OH + Cl^-$ (neomenthylchloride)	C_2H_5OH	$10^2A = 6.1$; $B = 1.5$	Na^+	= B	kAB	125	1.27	-3				*	(39a)
			9.9 0.36				125	1.45	-3					
			9.4 0.16				125	1.74	-3					
Hydroxy-substituted alkyl halide														
.141	$HOCH_2C(CH_3)_2CH_2Br + Ag^+ \longrightarrow C_2H_5(CH_3)CHCHO + AgBr + H^+$	Et 70*	A = 0.1; B = 0.14	NO_3^-	= B	k AB	92	7.1	-4				*	(1)
							109	3.05	-3	23.7	1	11		
.142	$CH_3C{:}OOCH_2C(CH_3)_2CH_2Br + Ag^+ + H_2O \longrightarrow C_2H_5(CH_3)CHCHO + AgBr + CH_3COOH + H^+$	Et 70*	A = 0.1; B = 0.14	NO_3^-	= B	k AB	92	3.7	-4				*	(1)
							109	1.49	-3	24	1	11		
Dicarboxy-substituted alkyl halide														
.143	l-$HOOCCH_2(COOH)CHCl + H_2O \longrightarrow HOOCCH{:}CHCOOH + H_3O^+ + Cl^-$	H_2O	A = 0.18	$HClO_4$	2	k A	50	1.27	-7				*(45) (46)	
					2		62	4.89	-7					
					2		75	1.92	-6					
					1		88	4.81	-6					
					2		88	6.70	-6	24.2	3.1	9		
					3		88	8.42	-6					
.144	l-$HOOCCH_2(COOH)CHBr + H_2O \longrightarrow HOOCCH{:}CHCOOH + H_3O^+ + Br^-$	H_2O	A = 0.18	$HClO_4$	2	k A	50	4.29	-7				*(45) (46)	
					2		62	1.63	-6					
					2		75	6.25	-6					
					1		88	2.32	-5					
					2		88	2.08	-5	24.0	8	9		
					3		88	2.00	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.145	$(CH_3)_3C(COONa)_2CBr + OH^- \longrightarrow$ $(CH_3)_2C{:}C(CH_3)COONa, CO_2, NaBr, (CH_3)_2CO, CH_3CH(COONa)_2$	H_2O	$10^2A = 4.7; B = 0.106$	Na^+		$k\,A$	48	4.59	-3				*	(35)
	Halogen-substituted alkyl halide													
.146	$FCH_2CH_2Br + OH^- \longrightarrow FCH{:}CH_2 + H_2O + Br^-$	D1W 50*	$10^2A = 1.8; 10^2B = 2.5$	Na^+	= B	$k\,AB$	30	5.0	-6				*	(38)
							70	9	-5					
.147	$ClCH_2CH_2Br + OH^- \longrightarrow ClCH{:}CH_2 + H_2O + Br^-$	D1W 50*	$10^2A = 1.8; 10^2B = 2.5$	Na^+	= B	$k\,AB$	30	2.21	-4				*	(38)
							70	1.22	-2	20.7	2	11		
.148	$BrCH_2CH_2Br + OH^- \longrightarrow CH_2{:}CHBr + H_2O + Br^-$	C_2H_5OH	$10A = 1.11; 10B = 2.07$	Na^+	= B	$k\,AB$	25	7.23	-4				*	(56)
			2.23 1.15				25	8.68	-4					
			2.34 1.02				35	2.88	-3					
			1.80 1.32				45	8.58	-3					
			0.93 4.42				55	1.97	-2					
			2.23 2.00				55	2.43	-2					
			2.48 1.00				55	2.78	-2	23.8				
			2.48 0.50				55	3.15	-2					
			2.48 0.25				55	3.70	-2					
			2.48 0.125				55	4.23	-2					
			0.10 0.015				55	5.12	-2					
		Et 90*	2.38				25	6.08	-4					
			2.09				55	1.68	-2	21.5				
		Et 75*	2.36				25	3.92	-4					
			2.32				55	7.53	-3	19				
		Et 50*	2.42				25	2.07	-4					
			2.32				55	4.20	-3	19.5				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.148	$BrCH_2CH_2Br + OH^- \longrightarrow$ *(continued)*	Et 25*	10B = 2.35	Na^+	= B	k AB	25	9.43	-5				*	(56)
			2.52				55	2.05	-3	20				
		Et 5*	2.40				25	4.53	-5					
			2.32				55	1.06	-3	20.5				
		D1W 50*	$10^2A = 1.8$; $10^2B = 2.5$				30	6.34	-4					(38)
							70	3.60	-2	20.8	7	11		
.149	$CH_3CHBr_2 + 2OH^- \longrightarrow CH_3CHO + H_2O + 2Br^-$	C_2H_5OH	$10^2A = 8$; $10^2B = 24$	Na^+	= B	k AB	25	1.85	-6				*	(56)
			4				55	1.60	-4					
			10				55	1.27	-4					
			24				55	1.14	-4	26				
.150	$BrCH_2C(CH_3)_2CH_2Br + H_2O + 2Ag^+ \longrightarrow$ $C_2H_5CH(CH_3)CHO + 2AgBr + 2H^+$	Et 70*	10A = 1; 10B = 2.8	NO_3^-	= B	k AB	92	4.2	-5					(1)
							109	1.75	-4	23	3	9		
.151	$CH_3(OH)CBr_2 + OH^- \longrightarrow CH_3C{:}OBr + H_2O + Br^-$	C_2H_5OH	$10^2A = 2$-4; $10B \simeq 2$	Na^+	= B	k AB	55	1.48	-2				*	(56)
	Substituted cyclo-alkyl halides													
.152	*trans-cyclo*-4-$OHC_6H_{10}Cl + H_2O \longrightarrow$	H_2O	$10^2A = 2$			k A	70	8.43	-6				*	(37)
							80	2.75	-5	28	1	13		
.153	*trans-cyclo*-4-$OHC_6H_{10}Cl + OH^- \longrightarrow$	H_2O	$10^2A = 2$; $10^2B = 9$-20	Na^+	= B	k AB	70	3.19	-4				*	(37)
							80	8.99	-4	24	1	12	$\Delta S^{\ddagger} = -2$	
.154	*trans-cyclo*-2-$(C_6H_5SO_2)C_6H_{10}Cl + OH^- \longrightarrow$	Et 80*	$10^3A = 3$-20; $10^3B = 4$-28	Na^+	= B	k AB	8	1.07	-2					(34)
							20	3.35	-2	16	2	10		
.155	*trans-cyclo*-2-$(p\text{-}CH_3C_6H_4SO_2)C_6H_{10}Cl + OH^- \longrightarrow$	Et 80*	$10^3A = 3$-20; $10^3B = 4$-28	Na^+	= B	k AB	8	6.44	-3					(34)
							20	2.11	-2	17	5	10		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.156	*trans-cyclo*-2-(p-$NO_2C_6H_4SO_2$)$C_6H_{10}Cl$ + OH^- ⟶	Et 80*	10^3A = 3-20; 10^3B = 4-28	Na^+	= B	k AB	8	1.34	-1					(34)
							20	4.03	-1	15	1	11		
.157	*trans-cyclo*-2-(p-$ClC_6H_4SO_2$)$C_6H_{10}Cl$ + OH^- ⟶	Et 80*	10^3A = 3-20; 10^3B = 4-28	Na^+	= B	k AB	1	1.08	-2					(34)
							10	2.55	-2					
							20	8.02	-2	16.5	1.6	11		
.158	*cyclo*-1,1-$C_6H_{10}Cl_2$ + H_2O ⟶	Et 80*	10^2A = 2-5			k A	50	7.9	-7				*	(33)
							80	2.5	-5	26	3	11	$\Delta S^{\ddagger}$ = -8	
.159	*cyclo*-1,1-$C_6H_{10}Cl_2$ + OH^- ⟶ C_6H_9Cl + H_2O + Cl^-	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB	80	7.55	-5					(33)
							100	5.32	-4	25	3	11	$\Delta S^{\ddagger}$ = -8	
.160	*cis-cyclo*-1,2-$C_6H_{10}Cl_2$ + OH^- ⟶ C_6H_9Cl + H_2O + Cl^-	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB	30	1.16	-5		$\Delta H^{\ddagger}$ = -22.9			(33)
							50	1.24	-4		$\Delta S^{\ddagger}$ = -6			
							80	2.83	-3	23.5	1	12		
.161	*trans-cyclo*-1,2-$C_6H_{10}Cl_2$ + $2OH^-$ ⟶ 1,3-C_6H_8 + $2H_2O$ + $2Cl^-$	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB = -dB/dt	80	9.1	-6				*	(33)
							100	7.2	-5	27	4	11	$\Delta S^{\ddagger}$ = -7	
.162	*cyclo*-1,1-$C_6H_{10}ClBr$ + OH^- ⟶ C_6H_9Cl + H_2O + Br^-	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB	30	1.66	-5		$\Delta H^{\ddagger}$ = 21.9			(33)
							50	1.62	-4		$\Delta S^{\ddagger}$ = -8			
							80	3.25	-3	22.5	3	11		
.163	*cis-cyclo*-1,2-$C_6H_{10}ClBr$ + H_2O ⟶	Et 80*	10^2A = 2-5			k A	100	~7	-7				*	(33)
.164	*cis-cyclo*-1,2-$C_6H_{10}ClBr$ + OH^- ⟶ C_6H_9Cl + H_2O + Br^-	Et 80*	10^2A = 1.5-3; B = 0.11	Na^+	= B	k AB	20	2.56	-4			$\Delta S^{\ddagger}$ = -9		(33)
							30	7.92	-4	20	2	11		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.165	*trans-cyclo*-1,2-$C_6H_{10}ClBr + H_2O \longrightarrow$	Et 80*	10^2A = 2-5			k A	100	< 1	-6				*	(33)
.166	*trans-cyclo*-1,2-$C_6H_{10}ClBr + 2OH^- \longrightarrow$ 1,3-$C_6H_8 + 2H_2O + Br^- + Cl^-$	Et 80*	10^2A= 1.5-3; B = 0.11	Na^+	= B	k AB= -dB/dt	80	3.15	-4			$\Delta S^{\ddagger}$= -9		(33)
							100	1.99	-3	24	2	11		
.167	*cyclo*-1,1-$C_6H_{10}Br_2 + H_2O \longrightarrow$	Et 80*	10^2A = 2-5			k A	80	1.07	-5				*	(33)
							100	7.59	-5	26	8	10		
				$LiClO_4$	0.11		80	1.20	-5			$\Delta S^{\ddagger}$= -10		
.168	*cyclo*-1,1-$C_6H_{10}Br_2 + OH^- \longrightarrow C_6H_9Br + H_2O + Br^-$	Et 80*	10^2A= 1.5-3; B = 0.11	Na^+	= B	k AB	30	1.36	-5			$\Delta H^{\ddagger}$= 22.3		(33)
							50	1.34	-4			$\Delta S^{\ddagger}$= -7		
							80	2.89	-3	22.9	4	11		
.169	*cis-cyclo*-1,2-$C_6H_{10}Br_2 + H_2O \longrightarrow$	Et 80*	10^2A = 2-5			k A	80	6.7	-8				*	(33)
							100	7.9	-7	33	1	13	$\Delta S^{\ddagger}$= -1	
.170	*cis-cyclo*-1,2-$C_6H_{10}Br_2 + OH^- \longrightarrow$ $C_6H_9Br + H_2O + Br^-$	Et 80*	10^2A= 1.5-3; B = 0.11	Na^+	= B	k AB	20	8.50	-4			$\Delta S^{\ddagger}$= -7		(33)
							30	2.61	-3	20	4	11		
.171	*trans-cyclo*-$C_6H_{10}Br_2 + H_2O \longrightarrow$	Et 80*	10^2A = 2-5			k A	80	1.32	-7					(33)
							100	1.06	-6	28	2	10	$\Delta S^{\ddagger}$= -15	
		M 99*					100	1.1	-7					
.172	*trans-cyclo*-$C_6H_{10}Br_2 + 2OH^- \longrightarrow$ 1,3-$C_6H_8 + 2H_2O + 2Br^-$	Et 80*	10^2A= 1.5-3; B = 0.11	Na^+	= B	k AB= -dB/dt	50	5.87	-5			$\Delta S^{\ddagger}$= -7		(33)
							80	1.36	-3	24	6	11		

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Unsaturated-Alkenyl halide													
.173	$CH_2{:}CHBr + OH^- \longrightarrow$	D1W 50*	$10^2A \simeq 2$; $10^2B = 2.5$	Na^+	= B	k AB	30	1.4	-7			$\Delta S^{\ddagger} = -11$		(38)
							75	2.7	-5	24.5	7	10		
.174	*cis*-$(COO^-)CH{:}C(COO^-)Cl + OH^- \longrightarrow$	H_2O	$10^2A \simeq 1$; $10^2B = 3$-7	$NaNO_3$	$\mu = 0.1$	k AB	70	8.09	-5		$\Delta S^{\ddagger} = -9$		*	(17) (36)
	(chloromaleate) $^-OOCC{:}CCOO^- + H_2O + Cl^-$				0		70	2.79	-5	24.9	2	11		(36)
		Et 54.2 wt*	7-16	$NaNO_3$	$\mu = 0.1$		70	8.32	-5			$\Delta S^{\ddagger} = -14$		(17) (36)
					0		70	8.8	-6	24.0	2	10		(36)
.175	*trans*-$(COO^-)CH{:}C(COO^-)Cl + OH^- \longrightarrow$	H_2O	$10^2A \simeq 1$; $10^2B = 3$-7	$NaNO_3$	$\mu = 0.1$	k AB	70	8.15	-4		$\Delta S^{\ddagger} = -16$		*	(17) (36)
	(chlorofumarate) $^-OOCC{:}CCOO^- + H_2O + Cl^-$				0		70	2.54	-4	21.0	6	9		(36)
		Et 54.2 wt*	7-16	$NaNO_3$	$\mu = 0.1$		70	9.96	-4		$\Delta S^{\ddagger} = -12$			(17) (36)
					0		70	8.45	-5	23.1	4	10		(36)
.176	*cis*-$(COO^-)CH{:}C(COO^-)Br + OH^- \longrightarrow$	H_2O	$10^2A \simeq 1$; $10^2B = 3$-7	$NaNO_3$	$\mu = 0.1$	k AB	70	1.13	-3			$\Delta S^{\ddagger} = -11$	*	(17) (36)
	(bromomaleate) $^-OOCC{:}CCOO^- + H_2O + Br^-$				0		70	3.84	-4	22.6	1	11		(36)
		Et 54.2 wt*	7-16	$NaNO_3$	$\mu = 0.1$		70	1.23	-3			$\Delta S^{\ddagger} = -13$		(17) (36)
					0		70	1.30	-4	22.5	3	10		(36)
.177	*trans*-$(COO^-)CH{:}C(COO^-)Br + OH^- \longrightarrow$	H_2O	$10^2A \simeq 1$; $10^2B = 3$-7	$NaNO_3$	$\mu = 0.24$	k AB	45	1.09	-4				*	(17)
	(bromofumarate) $^-OOCC{:}CCOO^- + H_2O + Br^-$				0.10		45	7.8	-5					
					0.055		45	6.6	-5					
					0.10		70	1.39	-2			$\Delta S^{\ddagger} = -19$		(17) (36)
					0		70	4.33	-3	17.9	1	9		(36)
		Et 54.2 wt*	7-16	$NaNO_3$	$\mu = 0.10$		70	2.04	-2			$\Delta S^{\ddagger} = -16$		(17) (36)
					0		70	1.92	-3	19.7	7	9		(36)
.178	*cis*-$ClCH{:}CHCl + OH^- \longrightarrow HC{:}CCl + H_2O + Cl^-$	C_2H_5OH	$10^2A = 2$-10; $10^2B = 2$-8	K^+	= B	k AB	50	1.7	-8				*	(42)
							75	6.3	-7					
							95	6.8	-6	31	1.8	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.179	*cis*-ClCH:CHCl + CH_3O^- ⟶ HC:CCl + CH_3OH + Cl^-	CH_3OH	10^3A = 6-160; 10^2B = 4-12	Na^+	= B	*k* AB	58	9.13	-6					(43)
							72	8.22	-5					
							85	5.13	-4	35.1	1.3	18		
.180	*trans*-ClCH:CHCl + OH^- ⟶ HC:CCl + H_2O + Cl^-	C_2H_5OH	10A = 1-2; 10B ≃ 1	K^+	= B	*k* AB	50	3.0	-9				*	(42)
							65	1.1	-8					
							75	3.4	-8					
							85	6.8	-8	20	1.1	5		
.181	*trans*-ClCH:CHCl + CH_3O^- ⟶ HC:CCl + CH_3OH + Cl^-	CH_3OH	10A = 2-16; 10B = 1-16	Na^+	= B	*k* AB	96	3.5	-7				*	(43)
							109	1.44	-6					
							122	6.0	-6			$\Delta S^{\ddagger}$ = -12		
							133	1.60	-5	29	6	10		
.182	*cis*-BrCH:CHBr + CH_3O^- ⟶ HC:CBr + CH_3OH + Br^-	CH_3OH	10^3A = 8-30; 10^2B = 1-38	Na^+	= B	*k* AB	24	1.18	-4				*	(43)
							35	6.03	-4			$\Delta S^{\ddagger}$ = +16		
							45	2.55	-3	28	5	16		
.183	*trans*-BrCH:CHBr + CH_3O^- ⟶ HC:CBr + CH_3OH + Br^-	CH_3OH	10^2A = 2-24; 10B = 1.5-6	Na^+	= B	*k* AB	79	5.9	-7				*	(43)
							94	4.2	-6			$\Delta S^{\ddagger}$ = +5		
							109	2.55	-5	33.4	3	14		
.184	CH_2:CBr_2 + OH^- ⟶ HC:CBr + H_2O + Br^-	C_2H_5OH		Na^+	= B	*k* AB	55	3.9	-4				*	(56)
.185	BrCH:CBr_2 + OH^- ⟶ BrC:CBr + H_2O + Br^-	C_2H_5OH	10^2A = 4; B = 0.24	Na^+	= B	*k* AB	25	2.6	-3				*	(56)
.186	*cis*-ICH:CHI + CH_3O^- ⟶ HC:CI + CH_3OH + I^-	CH_3OH	10^2A = 1-3; 10^2B = 1-3	Na^+	= B	*k* AB	0	3.90	-4				*	(43)
							25	1.78	-2	24.7	2	16	$\Delta S^{\ddagger}$ = +14	

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.187		*trans*-ICH:CHI + CH_3O^- ⟶ HC:CI + CH_3OH + I^-	CH_3OH	10^3A= 9-35; 10^3B= 4-21	Na^+	= B	*k* AB	58	8	-6				*	(43)
								69	5.1	-5			$\Delta S^{\ddagger}$= +24		
								83	4.0	-4	36	5	18		
Aryl-substituted aliphatic halide															
.188	.24	$C_6H_5CH_2CH_2Br$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 5; B= 0.10	Na^+	= B	*k* AB	30	4.17	-4				(29) (50)	
		$C_6H_5CH{:}CH_2$ + C_2H_5OH + Br^-						41	1.33	-3			$\Delta H^{\ddagger}$= 19.6	(50)	
								50	3.42	-3			$\Delta S^{\ddagger}$= -9.2		
								59	8.14	-3	20.2	1.5	11		
.189		$C_6H_5CH_2CH_2I$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 6; B= 0.12	Na^+	= B	*k* AB	30	2.66	-3					(29)
		$C_6H_5CH{:}CH_2$ + C_2H_5OH + I^-													
.190		*p*-$CH_3C_6H_4CH_2CH_2Br$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 5; B= 0.10	Na^+	= B	*k* AB	41	7.50	-4			$\Delta H^{\ddagger}$= 20.3		(50)
		p-$CH_3C_6H_4CH{:}CH_2$ + C_2H_5OH + Br^-						50	2.02	-3			$\Delta S^{\ddagger}$= -8.2		
								59	4.94	-3	20.9	3	11		
.191		*p*-$CH_3OC_6H_4CH_2CH_2Br$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 6; B= 0.12	Na^+	= B	*k* AB	30	1.73	-4					(29)
		p-$CH_3OC_6H_4CH{:}CH_2$ + C_2H_5OH + Br^-		5 .10				41	5.28	-4			$\Delta H^{\ddagger}$= 20.8		(50)
								50	1.51	-3			$\Delta S^{\ddagger}$= -7.3		
								59	3.78	-3	21.4	5	11		
.192		*p*-$CH_3OC_6H_4CH_2CH_2I$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 6; B= 0.12	Na^+	= B	*k* AB	30	9.56	-4					(29)
		p-$CH_3OC_6H_4CH{:}CH_2$ + C_2H_5OH + I^-													
.193		*p*-$CH_3C{:}OC_6H_4CH_2CH_2Br$ + $C_2H_5O^-$ ⟶	C_2H_5OH	10^2A= 5; B= 0.10	Na^+	= B	*k* AB	0	1.35	-3			$\Delta H^{\ddagger}$= 17.6		(50)
		p-$CH_3C{:}OC_6H_4CH{:}CH_2$ + C_2H_5OH + Br^-						10	4.64	-3			$\Delta S^{\ddagger}$= -7.0		
								20	1.34	-2	18.2	5	11		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.194	$p\text{-}NO_2C_6H_4CH_2CH_2Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 5$; $B = 0.10$	Na^+	= B	k AB	0	2.68	-2			$\Delta S^{\ddagger} = -0.8$		(50)
	$p\text{-}NO_2C_6H_4CH{:}CH_2 + C_2H_5OH + Br^-$						10	9.14	-2	18	1	13		
.195	$p\text{-}ClC_6H_4CH_2CH_2Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 6$; $B = 0.12$	Na^+	= B	k AB	30	1.90	-3			$\Delta H^{\ddagger} = 18.7$		(29) (50)
	$p\text{-}ClC_6H_4CH{:}CH_2 + C_2H_5OH + Br^-$		5 0.10				41	5.85	-3			$\Delta S^{\ddagger} = -9.2$		(50)
							50	1.41	-2	19.3	2	11		
.196	$p\text{-}ClC_6H_4CH_2CH_2I + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 6$; $B = 0.12$	Na^+	= B	k AB	30	1.05	-2					(29)
	$p\text{-}ClC_6H_4CH{:}CH_2 + C_2H_5OH + I^-$													
.197	$m\text{-}BrC_6H_4CH_2CH_2Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 6$; $B = 0.12$	Na^+	= B	k AB	30	3.71	-3					(29)
	$m\text{-}BrC_6H_4CH{:}CH_2 + C_2H_5OH + Br^-$													
.198	$m\text{-}BrC_6H_4CH_2CH_2I + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 6$; $B = 0.12$	Na^+	= B	k AB	30	2.03	-2					(29)
	$m\text{-}BrC_6H_4CH{:}CH_2 + C_2H_5OH + I^-$													
	Di-aryl-substituted aliphatic halide													
.199	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 4\text{-}8$; $B = 1\text{-}2$	Na^+	= B	k AB	50	3.29	-6				*	(11)
	trans-$CH_3(C_6H_5)C{:}CHC_6H_5 + C_2H_5OH + Cl^-$						75	4.48	-5					
		$(CH_3)_3COH$	7 0.9	K^+	= B		75	3.10	-5					
.200	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + (CH_3)_3CO^- \longrightarrow$ (*trans*)	$(CH_3)COH$	$10^2A = 5\text{-}7$; $B = 0.86$	K^+	= B	k AB	50	2.93	-6				*	(11)
			0.86				75	4.50	-5					
			0.60				75	3.76	-5					
.201	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + C_2H_5(CH_3)_2CO^- \longrightarrow$ (*trans*)	M	$10^2A = 7$; $B = 0.7$	K^+	= B	k AB	75	4.95	-5				*	(11)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.202	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + n\text{-}C_8H_{17}O^- \longrightarrow$ (*trans*)	M	$10^2A = 7$; B = 0.93	Na^+	= B	*k* AB	75	1.14	-6				*	([11])
			0.85				75	1.41	-6					
			0.50				75	2.83	-6					
.203	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + n\text{-}C_6H_{13}(CH_3)CHO^- \longrightarrow$ (*trans*)	M	$10^2A = 7.5$; B = 1.08	K^+	= B	*k* AB	75	1.80	-5				*	([11])
		C_6H_6	7 0.12	K^+	= B		75	3.3	-4					
.204	*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + C_2H_5O^- \longrightarrow$	C_2H_5OH	$10^2A = 3\text{-}7$; B = 1-2	Na^+	= B	*k* AB	50	2.96	-6				*	([11])
	cis-$CH_3(C_6H_5)C{:}CHC_6H_5 + C_2H_5OH + Cl^-$						75	4.32	-5					
		$(CH_3)_3COH$	7 1.1	K^+	= B		75	8.6	-6					
.205	*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + (CH_3)_3CO^- \longrightarrow$ (*cis*)	$(CH_3)_3COH$	$10^2A = 7$; B = 0.77	K^+	= B	*k* AB	75	4.04	-6				*	([11])
			.92				75	4.37	-6					
			1.28				75	5.55	-6					
			.92				100	5.14	-5					
			1.28				101	7.4	-5					
.206	*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + C_2H_5(CH_3)_2CO^- \longrightarrow$ (*cis*)	M	$10^2A = 7$; B = 0.70	K^+	= B	*k* AB	75	4.60	-6				*	([11])
.207	*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + n\text{-}C_8H_{17}O^- \longrightarrow$ (*cis*)	M	$10^2A = 4$; B = 0.93	Na^+	= B	*k* AB	75	1.25	-6				*	([11])
			7 0.85				75	1.51	-6					
.208	*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHCl + n\text{-}C_6H_{13}(CH_3)CHO^- \longrightarrow$ (*cis*)	M	$10^2A = 7.5$; B = 1.08	Na^+	= B	*k* AB	75	5.10	-6				*	([11])
		C_6H_6	7 0.12	K^+	= B		75	6	-5					
.209	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHBr + C_2H_5O^- \longrightarrow$ (*trans*)	EtB*	$10^2A = 3.7$; B = 0.61	Na^+	= B	*k* AB	50	2.10	-4				*	([11])
.210	*threo*-$CH_3(C_6H_5)CH(C_6H_5)CHBr + (CH_3)_3CO^- \longrightarrow$ (*trans*)	$(CH_3)_3COH$	$10^2A = 3.7$; B = 0.57	K^+	= B	*k* AB	50	6.6	-5				*	([11])

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.211		*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHBr + C_2H_5O^- \longrightarrow$ *(cis)*	EtB*	$10^2A = 3.7$; $B = 0.61$	Na^+	= B	kAB	50	3.0	-4				*	(11)
.212		*erythro*-$CH_3(C_6H_5)CH(C_6H_5)CHBr + (CH_3)_3CO^- \longrightarrow$ *(cis)* $(CH_3)_3COH$		$10^2A = 3.7$; $B = 0.57$	K^+	= B	kAB	50	1.22	-5				*	(11)
.213	.33	$(p\text{-}ClC_6H_4)_2CHCH_2Cl + OH^- \longrightarrow$ $(p\text{-}ClC_6H_4)_2C{:}CH_2 + H_2O + Cl^-$	Et 92.6 wt*	$10^3A = 5\text{-}10$; $10^2B = 5\text{-}6$	Na^+	= B	kAB	20 30 40	9.1 2.82 8.49	-4 -3 -3	20.2	1.1	$\Delta S^{\ddagger} = -5.8$ 12		(12) (22)
.214		$(p\text{-}BrC_6H_4)_2CHCH_2Cl + OH^- \longrightarrow$ $(p\text{-}BrC_6H_4)_2C{:}CH_2 + H_2O + Cl^-$	Et 92.6 wt*	$10^3A = 5\text{-}10$; $10^2B = 5.6$	Na^+	= B	kAB	20 30 40	1.26 4.06 1.17	-3 -3 -2	20.2	1.5	$\Delta S^{\ddagger} = -5.0$ 12		(12) (22)
.215		$(C_6H_5)_2CHCHCl_2 + OH^- \longrightarrow (C_6H_5)_2C{:}CHCl + H_2O + Cl^-$	Et 92.6 wt*	$10^2A = 1$; $10^2B = 5.3$	Na^+	= B	kAB	20 30 40	1.43 5.11 1.62	-4 -4 -3	21.9	3	$\Delta S^{\ddagger} = -3.4$ 12		(12) (22)
.216		$(p\text{-}CH_3C_6H_4)_2CHCHCl_2 + OH^- \longrightarrow$ $(p\text{-}CH_3C_6H_4)_2C{:}CHCl + H_2O + Cl^-$	Et 92.6 wt*	$10^2A = 1$; $10^2B = 5.3$	Na^+	= B	kAB	20 30 40	4.33 1.57 5.10	-5 -4 -4	22.3	1.9	$\Delta S^{\ddagger} = -4.4$ 12		(12) (22)
.217		$(p\text{-}CH_3OC_6H_4)_2CHCHCl_2 + OH^- \longrightarrow$ $(p\text{-}CH_3OC_6H_4)_2C{:}CHCl + H_2O + Cl^-$	Et 92.6 wt*	$10^2A = 1$; $10^2B = 5.3$	Na^+	= B	kAB	20 30 40	3.36 1.26 4.27	-5 -4 -4	23.0	5	$\Delta S^{\ddagger} = -2.5$ 12		(12) (22)
.218		$(p\text{-}FC_6H_4)_2CHCHCl_2 + OH^- \longrightarrow$ $(p\text{-}FC_6H_4)_2C{:}CHCl + H_2O + Cl^-$	Et 92.6 wt*	$10^2A = 1$; $10^2B = 5.3$	Na^+	= B	kAB	20 30 40	7.10 2.35 7.74	-4 -3 -3	21.6	9	$\Delta S^{\ddagger} = -1.3$ 12		(12) (22)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.219	.34	$(p\text{-}ClC_6H_4)_2CHCHCl_2 + OH^- \longrightarrow$	Et 92.6 wt.*	10^3A=4-10;	Na^+	=B	kAB	20	5.68	-3					(12) (22)
		$(p\text{-}ClC_6H_4)_2C{:}CHCl + H_2O + Cl^-$		10^2B=2-5				30	1.68	-2			$\Delta S^{\ddagger}$= -2.3		
								40	5.24	-2	20.1	5	12		
.220		$(p\text{-}BrC_6H_4)_2CHCHCl_2 + OH^- \longrightarrow$	Et 92.6 wt.*	10^3A=4-10;	Na^+	=B	kAB	20	7.76	-3					(12) (22)
		$(p\text{-}BrC_6H_4)_2C{:}CHCl + H_2O + Cl^-$		10^2B=2-5				30	2.38	-2			$\Delta S^{\ddagger}$= 0.0		
								40	7.57	-2	20.6	1.8	13		
.221	.26	$(C_6H_5)_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	10^2A=1;	Na^+	=B	kAB	20	3.69	-4					(12) (22)
		$(C_6H_5)_2C{:}CCl_2 + H_2O + Cl^-$		10^2B=4.7				30	1.27	-3			$\Delta S^{\ddagger}$=-6.5		
								40	3.51	-3	20.5	7	11		
.222	.27	$(p\text{-}CH_3C_6H_4)_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	10^2A=1;	Na^+	=B	kAB	20	1.09	-4					(12) (22)
		$(p\text{-}CH_3C_6H_4)_2C{:}CCl_2 + H_2O + Cl^-$		10^2B=5.3				30	3.69	-4			$\Delta S^{\ddagger}$=-7.1		
								40	1.11	-3	21.0	5	11		
.223	.29	$[p\text{-}(CH_3)_3CC_6H_4]_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	10^3A=5;	Na^+	=B	kAB	20	1.07	-4					(12) (22)
		$[p\text{-}(CH_3)_3CC_6H_4]_2C{:}CCl_2 + H_2O + Cl^-$		10^2B=4.7				30	3.37	-4	20	6	10		
.224	.28	$(p\text{-}CH_3OC_6H_4)_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	10^3A=9;	Na^+	=B	kAB	20	9.18	-5					(12) (22)
		$(p\text{-}CH_3OC_6H_4)_2C{:}CCl_2 + H_2O + Cl^-$		10^2B=4.7				30	3.03	-4			$\Delta S^{\ddagger}$=-6.1		
								40	9.72	-4	21.4	8	11		
.225	.32	$(p\text{-}FC_6H_4)_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	10^2A=1;	Na^+	=B	kAB	20	3.03	-3					(12) (22)
		$(p\text{-}FC_6H_4)_2C{:}CCl_2 + H_2O + Cl^-$		10^2B=4.7				30	9.4	-3			$\Delta S^{\ddagger}$=-4.6		
								40	2.67	-2	19.8	1.8	12		
.226	.35	$(p\text{-}ClC_6H_4)_2CHCCl_3 + OH^- \longrightarrow$	Et 76 wt.*	10^3A=5-10;	Na^+	=B	kAB	20	1.32	-2					(12) (22)
		$(p\text{-}ClC_6H_4)_2C{:}CCl_2 + H_2O + Cl^-$	" 87 "	10^2B=1-5				20	1.89	-2					
			" 92.6 "					20.1	2.48	-2			$\Delta S^{\ddagger}$=-5.5		
			" 92.6 "					30.4	7.11	-2	18	1	12		

Supplement 1958

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.227	.36	$C_6H_5(p\text{-}ClC_6H_4)CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	$10^2A=1$;	Na^+	=B	kAB	20.1	3.01	-3					(12) (22)
		$C_6H_5(p\text{-}ClC_6H_4)C{:}CCl_2 + H_2O + Cl^-$		$10^2B=4.7$				30.4	9.04	-3	19	5	11		
.228		$(o\text{-}ClC_6H_4)(p\text{-}ClC_6H_4)CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	$10^2A=1$;	Na^+	=B	kAB	20.1	3.71	-4					(12) (22)
		$(o\text{-}ClC_6H_4)(p\text{-}ClC_6H_4)C{:}CCl_2 + H_2O + Cl^-$		$10^2B=4.7$				30.4	1.21	-3	20	6	11		
.229	.37	$(p\text{-}BrC_6H_4)_2CHCCl_3 + OH^- \longrightarrow$	Et 92.6 wt.*	$10^3A=2\text{-}5$;	Na^+	=B	kAB	20	3.47	-2					(12) (22)
		$(p\text{-}BrC_6H_4)_2C{:}CCl_2 + H_2O + Cl^-$		$10^2B=1\text{-}2$				30	1.03	-1			$\Delta S^{\ddagger}=-3$		
								35	1.70	-1	18.8	4	12		
		Aryl-substituted unsaturated alkenyl halide													
.230		*cis*-$C_6H_5CH{:}CHBr + OH^- \longrightarrow C_6H_5C{\vdots}CH + H_2O + Br^-$	$(CH_3)_2CHOH$	$10^2A=1$;	Na^+	=B	kAB	22	2.84	-4					(25)
				$10^2B=10$											
				10				32	9.22	-4					
				6.7				43	3.16	-3			$\Delta S^{\ddagger}=-5.6$		
				12				43	2.84	-3	21.1	1.2	12		
.231		*cis*-$C_6H_5CH{:}CHBr + 2C_6H_5Li \longrightarrow$	$(n\text{-}C_4H_9)_2O$	$10^2A=3$;			kAB	2	3.81	-3				*	(23)
		$C_6H_5C{\vdots}CLi + 2C_6H_6 + LiBr$		$10B=1\text{-}2$											
.232		*trans*-$C_6H_5CH{:}CHBr + OH^- \longrightarrow$	$(CH_3)_2CHOH$	$10B=3.4$	Na^+	=B	kAB	98	2.28	-5				*	(25)
		$C_6H_5C{\vdots}CH + Br^- + H_2O$		$10^2A=1$; 1.7				98	2.43	-5					
				3.8				107	6.64	-5					
				1.9				107	7.61	-5					
				3.8				118	2.11	-4			$\Delta S^{\ddagger}=+4$		
				1.9				118	2.55	-4	31.8	1.3	14		

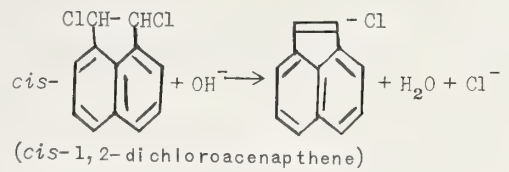
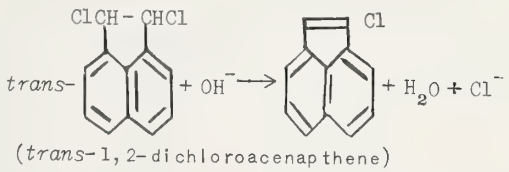
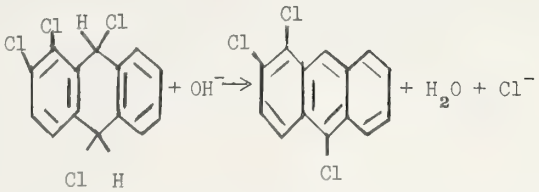
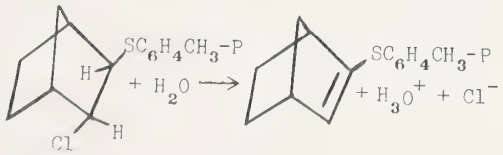
No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.233		*trans*-$C_6H_5CH{:}CHBr + 2C_6H_5Li \longrightarrow$	$(n\text{-}C_4H_9)_2O$	$10^2A=3$; $10^2B=6-12$			kAB	2	2.11	-2				*	(23)
		$C_6H_5C{\vdots}CLi + 2C_6H_6 + LiBr$													
.234		*cis*-*p*-$NO_2C_6H_4CH{:}CHBr + OH^- \longrightarrow$	$(CH_3)_2CHOH$	$10^3A=3$; $10^3B=13$	Na^+	=B	kAB	2	6.07	-2					(25)
		p-$NO_2C_6H_4C{\vdots}CH + H_2O + Br^-$		7.7				2	6.28	-2					
				7.7				10	1.73	-1			$\Delta S^{\ddagger}=-4.0$		
				7.6				22	5.24	-1	17.1	2	12		
			Et 92.6 wt.*	$10^3A=4-10$;				11	2.62	-3					(18)
				$10^2B=2-6$				20	9.77	-3					
								25	1.88	-2			$\Delta S^{\ddagger}=+12$		
								30	3.69	-2	23.9	6	15		
.235		*trans*-*p*-$NO_2C_6H_4CH{:}CHBr + OH^- \longrightarrow$	$(CH_3)_2CHOH$	$10^2A=1$; 10B=1-2			kAB	43	2.46	-4				*	(25)
		p-$NO_2C_6H_4C{\vdots}CH + H_2O + Br^-$		2				50	4.58	-4					
				1				61	1.68	-3			$\Delta S^{\ddagger}=-10$		
				1.8				61	1.53	-3	21.3	1.1	10		
			Et 92.6 wt.*	$10^3A=7-8$; $10^2B=8.6$	Na^+	=B		30	1.70	-5					(18)
								35	3.09	-5			$\Delta S^{\ddagger}=-4$		
								40	5.77	-5	23.8	2	12		
		Aromatization													
.236	.38	*α*-$C_6H_6Cl_6 + 3OH^- \longrightarrow$	Et 76.1 wt.*	$10^4A=4-10$;	Na^+	=B	kAB =	1.1	1.9	-2			$\Delta S^{\ddagger}=-1.0$		(15) (21) (57)
		(aaeeee configuration)		$10^3B=3-10$			$-dA/dt$	20.1	1.70	-1	18.5	1	13	*	
		$C_6H_3Cl_3 + 3H_2O + 3Cl^-$	Et 92.6 wt.*	$10^4A=4-10$;				-0.3	2.43	-2			$\Delta S^{\ddagger}=0$		(15) (21)
		products 1,2,3-17%		$10^3B=3-10$				16.2	1.77	-1	18.6	2	13	*	
		1,2,4-76%	Et 97.6 wt.*	$10^4A=4-10$;				7.1	7.7	-2					
		1,3,5-7%		$10^3B=3-10$				14.4	1.67	-1			$\Delta S^{\ddagger}=+6$		
								22.5	4.95	-1	20.0	3	14		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.236	.38	α-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ *(continued)*	Et 80*	$10^3A \simeq 2$; $10^2B \simeq 1$	Na^+	=B	$kAB =$	0	1.50	-2				*	(39)
			Et 90*				$-dA/dt$	-15	2.3	-3					
								-9	7.05	-3					
								0	2.00	-2					
								14	1.09	-1					
								20	2.28	-1	19.0	3	13		
			C_2H_5OH					0	3.12	-2					
.237	.39	α-$C_6H_6Cl_6 + OH^- \longrightarrow$ $C_6H_5Cl_5 + H_2O + Cl^-$	See reaction (.236)		Na^+	=B								*	(15) (21) (39)
.238	.41	β-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ (eeeeee configuration) $C_6H_3Cl_3 + 3H_2O + 3Cl^-$ products 1, 2, 3-4.6% 1, 2, 4-86% 1, 3, 5-9%	Et 76.1 wt.*	10^4A=4-40; 10^2B=2-9	Na^+	=B	$kAB =$	30.6	2.30	-5			$\Delta S^{\ddagger}$=+20		(15) (21) (57)
							$-dA/dt$	50.0	4.71	-4	30.9	4	17	*	
			Et 81.5 wt.*					30-50			30.6		$\Delta S^{\ddagger}$=+19		
			Et 89.0 wt.*					30-50			31.4			+22	
			Et 91.2 wt.*					30-50			31.1			+21	
			Et 92.6 wt.*					30.6	2.23	-5			$\Delta S^{\ddagger}$=+27		
								50.0	6.16	-4	33.1	2	19		
			Et 94.1 wt.*					30-50			32.1		$\Delta S^{\ddagger}$=+24		
			Et 97.6 wt.*					30.6	1.97	-5			$\Delta S^{\ddagger}$=+22		
								50.0	4.67	-4	31.7	1	18		
			Et 80*	$10^3A \simeq 2$; $10^2B \simeq 1$			$kAB =$	77	2.38	-2					(39)
							$-dA/dt$	90	1.21	-1	32.3	3	18		
			Et 90*					55	1.37	-3					
								61	3.19	-3					
								68	8.70	-3					
								77	3.01	-2					
								90	1.49	-1	32.3	4	18		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.238	.41	β-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ *(continued)*	C_2H_5OH	$10^3A \simeq 2$; $10^2B \simeq 1$	Na^+	= B	$kAB =$	77	2.73	-2				*	(39)
							$-dA/dt$	90	1.36	-1	33	1	19		
.239	.42	β-$C_6H_6Cl_6 + OH^- \longrightarrow$ β-$C_6H_5Cl_5 + H_2O + Cl^-$	See reaction (.238)		Na^+	= B								*	(15) (21) (39)
.240	.43	γ-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ (aaaeee configuration) $C_6H_3Cl_3 + 3H_2O + 3Cl^-$ products 1,2,3-4.6% 1,2,4-81% 1,3,5-14%	Et 76.1 wt.*	10^4A=5-10; 10^3B=4-10	Na^+	= B	$kAB =$	10.1	1.44	-2				*	(15) (21) (57)
							$-dA/dt$	20.1	4.5	-2		$\Delta S^{\ddagger}$	=+3.6		
								29.7	1.51	-1	20.6	1.1	14		
			Et 80*	$10^3A \simeq 2$; $10^2B \simeq 1$			$-dA/dt = kAB$	14	5.27	-2				*	(39)
			Et 90*				$-dB/dt = kAB + 2k'A'B$	-8.5	3.12	-3					
							for k' see reaction (.251)	0	1.12	-2					
								7	2.74	-2					
								14	6.85	-2					
								20	1.46	-1	20.4	2.5	14		
			C_2H_5OH					14	9.67	-2					
.241	.44	γ-$C_6H_6Cl_6 + OH^- \longrightarrow$ $C_6H_5Cl_5 + H_2O + Cl^-$	See reaction (.240)		Na^+	= B								*	(15) (21) (39)
.242	.46	δ-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ (aeeeee configuration) $C_6H_3Cl_3 + 3H_2O + 3Cl^-$ products 1,2,3-5% 1,2,4-86% 1,3,5-9%	Et 76.1 wt.*	10^4A=3-10; 10^3B=3-5	Na^+	= B	$-dA/dt = kAB$	20	1.1	-1				*	(13) (39)
			Et 80*	$10^3A \simeq 2$; $10^2B \simeq 1$			$-dA/dt = kAB$	-15	1.10	-2					
			Et 90*				$-dB/dt = kAB + 2k'A'B$	-27	1.86	-3					
							for k' see reaction (.252)	-21	5.08	-3					
								-15	1.48	-2					
								-8	4.51	-2	21.6	2.5	16		
			C_2H_5OH					-15	1.20	-2					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.243	.47	δ-$C_6H_6Cl_6 + OH^- \longrightarrow C_6H_5Cl_5 + H_2O + Cl^-$	See reaction (.242)		Na^+	=B									(13) (39)
.244	.51	ϵ-$C_6H_6Cl_6 + 3OH^- \longrightarrow$ (aeeaee configuration) $C_6H_3Cl_3 + 3H_2O + 3Cl^-$ products 1,2,3-5% 1,2,4-95% 1,3,5- 0	Et 76.1 wt.*	10^4A=5-20; 10^3B=5-18	Na^+	=B	$-dA/dt = kAB$	10.1	1.42	-2				*	(15) (21)
								20.3	5.65	-2			$\Delta S^{\ddagger} = +6.5$		
								29.7	1.70	-1	21.4	5	14		
			Et 92.6 wt.*					10.4	1.47	-2					
								22.5	8.07	-2			$\Delta S^{\ddagger} = +10$		
								30.6	2.03	-1	22.3	2	15		
.245		ϵ-$C_6H_6Cl_6 + OH^- \longrightarrow C_6H_5Cl_5 + H_2O + Cl^-$	See reaction (.244)		Na^+	=B								*	(15) (21)
.246		α-$C_6H_6Cl_4 + 2OH^- \longrightarrow C_6H_4Cl_2 + 2H_2O + 2Cl^-$	Et 80*	10^2A=1; 10^2B=2	Na^+		$-dA/dt = kAB$	29	7.18	-3				*	(47)
.247		α-$C_6H_6Cl_4 + 2C_6H_5O^- \longrightarrow$ (eeaa configuration) $C_6H_4Cl + 2C_6H_5OH + 2Cl^-$ 47.8% o-, 50.4% m-, 1.8% p-	Et 80*		Na^+		$-dA/dt = kAB$	29	~1	-3				*	(47)
.248		α-$C_6H_6Cl_4 + C_5H_{10}NH \longrightarrow$ (eeaa configuration)	Et 80*					29	0					*	(47)
.249		β-$C_6H_6Cl_4 + 2OH^- \longrightarrow$ (aeea configuration) $C_6H_4Cl_2 + 2H_2O + 2Cl^-$ 2.9% o-, 31.1% m-, 66% p-	Et 80*	10^2A=1; 10^2B=2	Na^+		$-dA/dt = kAB$	29	6.67	-2				*	(47)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.250	γ-$C_6H_6Cl_4 + 2OH^- \longrightarrow C_6H_4Cl_2 + 2H_2O + 2Cl^-$	Et80*	$10^2A=1$; $10^2B=2$	Na^+	$-dA/dt = kAB$		29	2.72	-1				*	(47)
	(eeea configuration) 28.4% *o*-, 42.7% *m*-, 28.9% *p*-													
.251	δ-$C_6H_6Cl_4 + 2OH^- \longrightarrow C_6H_4Cl_2 + 2H_2O + 2Cl^-$	Et80*	$10^2A=1$; $10^2B=2$	Na^+	$-dA/dt = kAB$		29	1.20	-3				*	(47)
	(eeee configuration) 15.8% *o*-, 23.7% *m*-, 60.5% *p*-													
.252	ϵ-$C_6H_6Cl_4 + 2OH^- \longrightarrow C_6H_4Cl_2 + 2H_2O + 2Cl^-$	Et80*	$10^3A=2$; $10^3B=4$	Na^+	$-dA/dt = kAB$		29	8.33	0				*	(47)
	(eeae configuration) 7.5% *o*-, 25% *m*-, 67.5% *p*-													
.253	β-$C_6H_5Cl_5 + 2OH^- \longrightarrow C_6H_3Cl_3 + 2H_2O + 2Cl^-$	Et80*	$10^3A=2$; $10^3B=4$	Na^+	$-dA/dt = kAB$		29	5.72	0					(47)
.254	γ-$C_6H_5Cl_5 + 2OH^- \longrightarrow C_6H_3Cl_3 + 2H_2O + 2Cl^-$	Et80*	$10^3A=0-1$; $10^2B=1$	Na^+	$-dA/dt = kAB$		14	2.78	-2				*	(39)
		Et90*					0	5.92	-3					
							7	1.58	-2					
							14	4.00	-2					
							20	7.70	-2					
							28	1.92	-1	20.1	8	13		
		C_2H_5OH					14	5.18	-2					
.255	δ-$C_6H_5Cl_5 + 2OH^- \longrightarrow C_6H_3Cl_3 + 2H_2O + 2Cl^-$	Et80*	$10^3A=0-1$; $10^2B=1$	Na^+	$-dA/dt = kAB$		0	9.58	-3				*	(39)
	(eeeee configuration) products 1,2,3-5%		2 0.4				29	3.39	-1	20.3	1.7	14		(47)
	1,2,4-86%	Et90*	0-1 1				-8	3.56	-3					(39)
	1,3,5-9%						0	1.13	-2					
							14	7.78	-2					
							20	1.63	-1	21.1	1.0	15		
		C_2H_5OH					0	1.38	-2					
.256	γ-$C_6H_4Cl_6 + 2OH^- \longrightarrow C_6H_2Cl_4 + 2H_2O + 2Cl^-$	Et80*	$10^3A=2$; $10^3B=4$	Na^+	$=B$	$-dA/dt = kAB$	29	5.29	0					(47)
	(aaeeee configuration)													
	products 1,2,3,4-47.2%; 1,2,3,5-52.6%; 1,2,4,5-0.2%													

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.257	 (*cis*-1,2-dichloroacenapthene)	Et 92.6 wt.*	$10^3A \simeq 1$; $10^3B = 3-7$	Na^+	= B	*k* AB	3.2 10.5 22.1	1.77 5.32 1.98	-2 -2 -1	20.8	6	$\Delta S^{\ddagger} = 6.9$ 14		(26)
.258	 (*trans*-1,2-dichloroacenapthene)	Et 92.6 wt.*	$10^3A \simeq 1$; $10^3B = 3-7$	Na^+	= B	*k* AB	30.5 36.4 43.1	7.65 1.69 3.89	-4 -3 -3	24.8	6	$\Delta S^{\ddagger} = 6.9$ 14		(26)
.259	 (*trans*-1,8,9,10-tetrachloro-9,10-dihydroanthracene)	DEt*	$10^3A = 1-2$; $10^3B = 3-9$	Na^+	= B	*k* AB	6.4 10.5 18.1	1.47 2.64 5.50	-1 -1 -1	15.3	2	$\Delta S^{\ddagger} = -9$ 11		(16)
	Bridged-ring systems													
.260		Et 85 wt.*	$10^3A = 4-9$			*k* A	116	2.6	-5				*	(14)

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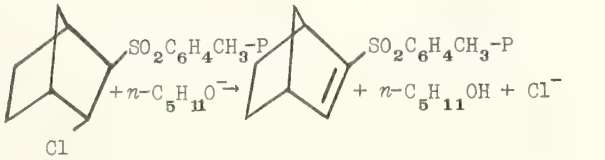
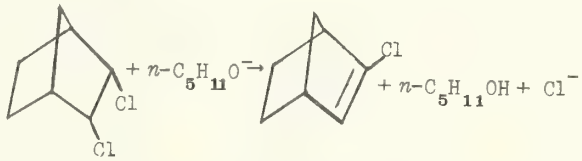
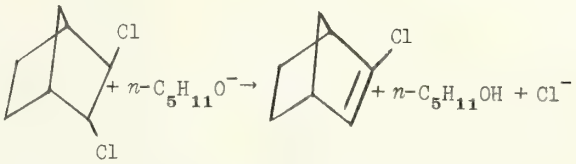
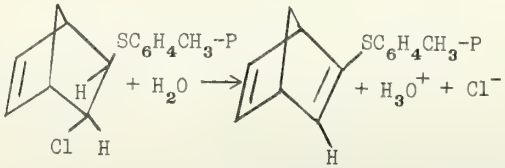
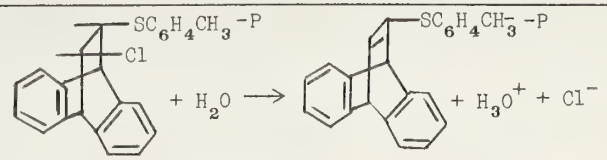
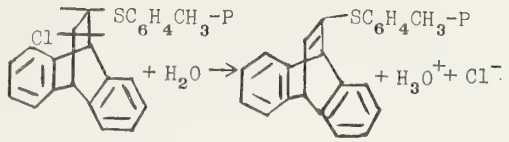
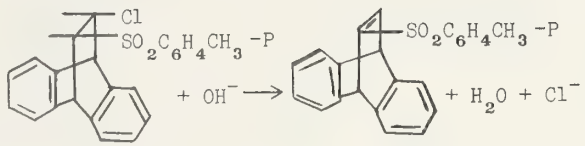
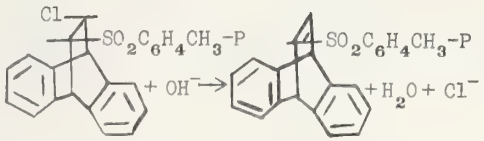
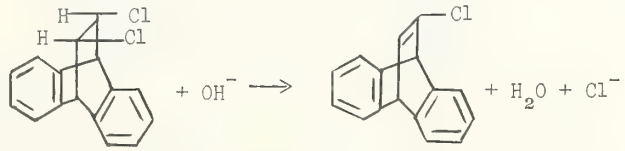
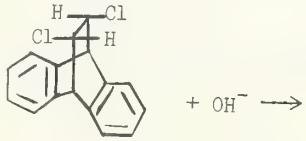
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.261	 (exo-2-*p*-toluenesulfonyl-endo-3-chloronorbornane)	$C_5H_{11}OH$	10^3A=7-15; 10^3B=9-24	Na^+	=B	*k*AB	0 12	4.91 2.16	-3 -2	19	8	12		(24)
.262	 endo-*cis*-2,3-dichloronorbornane)	$C_5H_{11}OH$	10^2A=2-3; 10B=2-4	Na^+	=B	*k*AB	101 116	1.01 5.0	-6 -6	31	1	12		(24)
.263	 (*trans*-2,3-dichloronorbornane)	$C_5H_{11}OH$	10^2A=1-3; 10B=7-23	Na^+	=B	*k*AB	101 116	6.6 3.4	-5 -4	32	4	14	*	(24)
.264		Et 85 wt.*	10^3A=4			*k*A	116	6.6	-6				*	(14)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.265		Et 85 wt.*	$10^3A=3$			kA	116	1.1	-6				*	(14)
.266		Et 85 wt.*	$10^3A=1-2$			kA	116	5.8	-6				*	(14)
.267		DE*	$10^3A\simeq2$; $10^3B=2-2.5$	Na^+	$=B$	kAB	0 12	2.65 9.65	0 0	16	3	13		(14)
.268		DE*	$10^3A=2-6$; $10^3B=2.5-4$	Na^+	$=B$	kAB	0 12	9.20 3.10	-1 0	15.6	3	12		(14)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.269	 ((*cis*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene)	DEW*	10^3A=9; 10B=2-4	Na^+	=B	*k*AB	102	3.01	-5				*	([20])
							110	6.42	-5					
							120	1.45	-4			$\Delta S^{\ddagger}$=-11.2		
							129	3.43	-4	26.5	8	10		
.270	 (*trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene)	DEW*	10^3A=9; 10B=2-4	Na^+	=B	*k*AB	91	5.70	-5				*	([20])
							102	2.18	-4					
							110	4.59	-4			$\Delta S^{\ddagger}$=+3.2		
							120	1.34	-3	30.6	1.5	14		

CODED SOLVENTS

Et50* (5, 25, 60, 70, 75, 80, 90, 95, 98)	C_2H_5OH (vol. % as indicated) + H_2O
BC85*	*n*-butyl cellosolve 85 volumes + 15 vol. H_2O
DiW50*	1,4-dioxane (vol. % as indicated) + H_2O
M99*	CH_3OH 99 wt. % + H_2O
Et X wt.*	C_2H_5OH + X wt. % H_2O
EtB*	C_2H_5OH 3 vol. + C_6H_6 2 vol.
DE*	Equal volumes of dioxane and C_2H_5OH 92.6% by weight
DEt*	75 volume % dioxane in 92.6 wt. % C_2H_5OH
DEW*	C_2H_5OH 40.5 wt.%, Dioxane 55.2 wt.%, H_2O 4.3 wt.%

COMMENTS

General: Elimination reaction frequently accompanied by parallel solvolysis reaction leading to substitution of hydroxyl or alkoxyl group for halogen. See 212.471. Both reactions may occur through same intermediate by removal of H^+ by base forming carbanion intermediate with either elimination or substitution of halogen following. For detailed discussion of mechanism of elimination and substitution reactions see ([31a]).

Classification: The aliphatic halides undergoing elimination are grouped under the headings: Saturated alkyl halide (.52)-(.119); Cyclo alkyl halide (.120)-(.140); Hydroxy-substituted alkyl halide (.141)(.142); Di-carboxy substituted alkyl halide (.143)-(.145); Halogen substituted alkyl halide (.146)-(.151); Substituted cycloalkyl halide (.152)-(.172); Unsaturated alkenyl halide (.173)-(.187); Aryl-substituted alkyl halide (.188)-(.198); Di-aryl substituted alkyl halide (.199)-(.229); Aryl-substituted unsaturated alkenyl halide (.230)-(.235); Aromatization (.236)-(.259); Bridged-ring systems (.260)-(.270).

Reaction: (.52) See 212.471, .183 for important parallel solvolysis reaction. (.53) See 212.471, .184 for important parallel solvolysis reaction. (.54) See 212.471, .185 for parallel solvolysis reaction. (.55) See 212.471, .186 for parallel solvolysis reaction. (.56) See 212.471, .187 for parallel solvolysis reaction. (.57) See 212.471, .188 for important parallel solvolysis reaction. (.58) See 212.471, .193 for important parallel solvolysis reaction. (.59) Products of reaction not determined. Reaction followed was formation of I^-. (.60) See 212.471, .194 for parallel solvolysis reaction. (.61) See 212.471, .195 for parallel solvolysis reaction. (.62) See 212.471, .196 for important parallel solvolysis reaction. (.63) See 212.471, .197 for parallel solvolysis reaction. (.64) See 212.471, .198 for parallel solvolysis reaction. (.65) Products of reaction not determined. Reaction followed was formation of I^-. (.66) See 212.471, .200 for parallel solvolysis reaction. (.67) Ratio of elimination to solvolysis not stated. Total rate measured. (.68) Rate constant corrected for thioether formation amounting to 7% of total reaction. (.69) Products of reaction not determined. (.70) See 212.471, .206 for important parallel solvolysis reaction. (.71) Initial rate only as reverse reaction important. In absence of $(C_2H_5)_4NCl$ no elimination observed. (.72) Products not identified except for 46% yield of isobutylene. (.73)(.74) Products not determined except yield if isobutylene varied between 85 and 100%. (.75) Rate law over course of reaction given by:

$$-dA/dt = k_1AB/(\alpha M + B)$$

where α was found to have an average value of 25. The initial rate giving value of rate constant k_1 in absence of added Br^-. (.76) See 212.471, .208 for important parallel solvolysis reaction. (.77) See 212.471, .210 for important parallel solvolysis reaction. (.78) See 212.471, .211 for important parallel solvolysis reaction. (.79) See 212.471, .213 for important parallel solvolysis reaction. (.80) Relative amount of parallel solvolysis and elimination reactions not determined. (.81) See 212.471, .215 for parallel solvolysis reaction. (.82) See 212.471, .216 for important parallel solvolysis reaction. (.83) See 212.471, .217 for parallel solvolysis reaction. (.84)

COMMENTS *(continued)*

See 212.471, .218 for parallel solvolysis reaction. Olefin analysis gave 71% $C_2H_5CH{:}CHCH_3$ and 29% $CH_3CH_2CH_2CH{:}CH_2$. (.85) See 212.471, .219 for important parallel solvolysis reaction. (.86) See 212.471, .220 for parallel solvolysis reaction. (.87) See 212.471, .221 for parallel solvolysis reaction. (.88) See 212.471, .223 for parallel solvolysis reaction. (.89) See 212.471, .224 for important parallel solvolysis reaction. Rate constant reported for ([7]) in 85% *n*-butyl cellosolve is total rate constant for both the elimination and solvolysis reactions. (.90) See 212.471, .225 for important parallel solvolysis reaction. (.91) See 212.471, .226 for important parallel solvolysis reaction. (.92) See 212.471, .227 for important parallel solvolysis reaction. (.93) Elimination reaction yields 80% 2-methyl-2-butene and 20% 2-methyl-1-butene. (.94) See 212.471, .232 for important parallel solvolysis reaction. At low $[C_2H_5O^-]$ 81.6% of 2-methyl-1-butene and 18.4% of 2-methyl-2-butene produced. At $[C_2H_5O^-]$ = 2.0 the % 2-methyl-1-butene is 71.9% with 28.1% of 2-methyl-2-butene. (.95) Elimination reaction yields 19% $(CH_3)_2CHCH_2CH{:}CH_2$ and 78% *trans*-$(CH_3)_2CHCH{:}CHCH_3$ and 3% *cis*-$(CH_3)_2CHCH{:}CHCH_3$. (.96) See 212.471, .238 for important parallel solvolysis reaction. (.97) Elimination reaction yields 71% 2-methyl-2-pentene and 29% 2-methyl-1-pentene. (.98) See 212.471, .239 for parallel solvolysis reaction. (.99) See 212.471, .240 for parallel solvolysis reaction. (.100) Elimination reaction yields 82% 2,3-dimethyl-2-butene and 18% 2,3-dimethyl-1-butene. (.101) See 212.471, .241 for important parallel solvolysis reaction. (.102) Elimination yields 96.5% of 3-methyl-2-pentene, (38.5% *cis*, 58.0% *trans*) and 3.5% of 2-ethyl-1-butene. (.103) Elimination reaction yields 21% 4,4-dimethyl-1-pentene, 77% *trans*-4,4-dimethyl-2-pentene and 2% *cis*-4,4-dimethyl-2-pentene. (.104) See 212.471, .242 for important parallel solvolysis reaction. (.105) Elimination reaction yields 59% 2,4-dimethyl-2-pentene and 41% 2,4-dimethyl-1-pentene. (.106) See 212.471, .244 for rate constant for total solvolysis and elimination reaction. (.107)(.108) Products of reaction not determined. Reaction followed was rate of production of chloride ion. (.109) See 212.471, .244 for rate constant for total solvolysis and elimination reaction. (.110) See 212.471, .245 for parallel solvolysis reaction. In *n*-butylcellosolve ([7]) finds rate constant for total solvolysis and elimination reaction to be 2.09×10^{-5}. In this solvent elimination yields 81% 2,4,4-trimethyl-1-pentene and 19% of 2,4,4-trimethyl-2-pentene. (.111) Elimination reaction yields 81% 2,4,4-trimethyl-1-pentene and 19% 2,4,4-trimethyl-2-pentene. (.112) See 212.471, .248 for rate constant for total solvolysis and elimination reaction. (.113) See 212.471, .250 for rate constant for total solvolysis and elimination reaction. (.114) See 212.471, .251 for rate constant for total solvolysis and elimination reaction. (.115)(.116) See 212.471, .253 for rate constants for total solvolysis and elimination reactions. (.117) First order rate law assumed from behavior in ethanol-water solvent. Pure chloride decomposes at room temperature. Prepared by saturating olefin at -40 °C. (.118)(.119) Only olefins produced no solvolysis to give alcohol or ether. (.120) (.121) Extent of olefin production not stated. (.123) See 212.471, .257 for parallel solvolysis reaction. (.124)

COMMENTS *(continued)*

(.125)(.126)(.127) Extent of elimination and parallel solvolysis not stated. (.128) See 332.771, .132 for parallel exchange reaction. (.132) Extent of elimination and parallel solvolysis not stated. (.133) Pseudo first order rate law followed after rapid reaction of trans-isomer in mixture, see .134 . Extrapolation to zero time used to determine relative amounts of isomers present. In mixture starting with 63% cis-isomer products were 50% 1,2-dimethylcyclohexene and 50% 2-methylene-methylcyclohexane. (.134) (.135) Pure trans-isomer yields exclusively 1,2-dimethylcyclohexene. (.136) Relative extent of elimination and solvolysis reactions not stated. (.137) Relative extent of elimination and solvolysis reactions not stated. No appreciable difference in rate for cis-rich or trans-rich isomer mixtures. (.138) See 212.471, .264 for parallel solvolysis reaction. (.139) See 212.471, .266 for parallel solvolysis reaction. (.140) See 212.471, .267 for parallel solvolysis reaction. (.141)(.142) Alcohol and ester yield same product L involving rearrangement. (.143) (.144) Values reported by ([45]) corrected by ([46]). (.145) Reaction followed was rate of formation of Br^-. Calculated first or second order constants for rate of disappearance of B decrease with progress of reaction. (.146) Elimination represents only about 9% of total reaction. Remaining 91% is parallel solvolysis. (.147) Rate constant for elimination reaction calculated from rate law for parallel reactions with different stoichiometry as solvolysis reaction consumes second mole of B for production of ethylene oxide. (.148) Rate constants of ([56]) include parallel solvolysis reaction in 18.5% yield compared to 79.5% of CH_2:CHBr. ([38]) calculated rate constant of elimination reaction separately by means of the difference in stoichiometry since solvolysis consumes two moles of B for each mole A reacting. Rate constants listed are actual rate constants not constant per halogen of ([38]). (.149) Rate constants are extrapolated to zero time since calculated constants decrease with progress of reaction. (.151) Reaction yields sodium acetate as final product but acetyl bromide considered to be product of rate determining step. (.152) Products of reaction are 84% cyclohexene-ol and 16% of a 1,4 oxide bridged cyclohexane. (.153) Products of reaction are less than 30% cyclohexene-ol and more than 70% of the 1,4 oxide bridged cyclohexane. (.158) Products of reaction not determined. Reaction probably complex involving elimination and solvolysis. Rate given is for production of HCl. Calculated constants drift with course of reaction. Values given should not be considered accurate. (.161) Reaction was so slow that alkali in glass was thought to complicate measurements. Value tabulated is for initial rate. (.163)(.165) Rate constant listed only approximate as calculated constants drifted seriously. Products of reaction not determined. (.167) Calculated rate constants drifted except in presence of $LiClO_4$. Products of reaction not determined. (.169) Products of reaction not determined. (.173) Elimination of first Cl^- considered to be rate determining step followed by rapid elimination of second and third Cl^-. (.174)(.175)(.176)(.177) Dependence upon ionic strength given by:

$$\log k = \log k_o + 4 S\sqrt{\mu}/(1 + A a\sqrt{\mu}), \text{ where}$$

$$S = 1.825 \times 10^6 (DT)^{-\frac{3}{2}} \; A = 50.30 \times 10^8 (DT)^{-1/2} \, cm^{-1}, a = 5.0 Å$$

COMMENTS *(continued)*

for cis-isomers and 4.0 Å for trans-isomers. Values at $\mu = 0$ are extrapolated values. (.178)(.180) Authors observed that rate based upon consumption of B was always lower than when based upon M produced. Attributed this to acidity of L. (.181) Calculated second order constant increased with progress of reaction. Rate constants extrapolated to zero ionic strength. (.182)(.183) Values extrapolated to zero ionic strength. (.184) Calculated second order constants drift with course of reaction. Negative salt effect apparent. (.185) Calculated second order constants decrease with course of reaction, (one third at $t_{1/2}$). Negative salt effect observed. (.186) Values extrapolated to zero ionic strength. (.187) Calculated second order constants increase with progress of reaction. HC:CI observed to undergo a subsequent disproportionation reaction:

$$2\,HC{:}CI \longrightarrow HC{:}CH + IC{:}CI.$$

(.199)-(.202) Second order rate constant calculated by dividing pseudo first order constant by concentration of B which was in excess. (.203) For reaction in:

$$n\text{-}C_6H_{13}(CH_3)CHOH$$

as solvent second order constant calculated from pseudo first order constant by dividing by concentration of B. In C_6H_6 as solvent true second order equation used and calculated constants decreased with progress of reaction. (.204)-(.207) Second order rate constant calculated by dividing pseudo first order constant by concentration of B which was in excess. (.208) For reaction in:

$$n\text{-}C_6H_{13}(CH_3)CHOH$$

as solvent second order constant calculated from pseudo first order constant by dividing by concentration of B. In C_6H_6 as solvent true second order equation used and calculated second order constants decreased with progress of reaction. (.209)-(.212) Second order rate constant calculated by dividing pseudo first order constant by concentration of B. (.231) Calculated second order rate constants fall rapidly beyond 40-60% reaction and were not reproducible. (.232) Good second order rate constants for first 75% reaction with only slight downward drift above 75% reaction. Addition of $NaClO_4$ had no effect showing negligible salt effect. (.233) Calculated second order rate constants fall rapidly beyond 40-60% reaction and were not reproducible. (.235) Final product in $(CH_3)_2CHOH$ is the diisopropyl acetal but authors consider elimination with formation of acetylene as rate determining step. In ethanol-water solvent the product is the diethyl acetal. Total reaction involves 3 moles of base per mole of halide. (.236) Reaction considered to involve three consecutive reactions with (.237) as the rate determining step followed by much more rapid elimination of second and third HCl. (.237) Considered to be rate determining step for (.236). (.238) Reaction considered to involve three consecutive reactions with (.239) as the rate determining step followed by much more rapid elimination of second and third HCl, see reaction (.253). (.239) Considered to be rate determining step for (.238). (.240) Reaction considered to involve three consecutive steps with (.241) and (.254) considered by ([39]) to be rate controlling. Rate constant for first step evaluated from initial rates. Composite rate data used to evaluate k' for second step as well as reaction of isolated intermediate see reaction (.254). (.241) Con-

COMMENTS *(continued)*

sidered to be one of two rate controlling steps for reaction (.240). See also (.254). (.242) Considered to involve three consecutive steps with rate being controlled by (.243) and (.255). Rate constant for first step evaluated from initial rates. Rate constant for second step evaluated from reaction of isolated intermediate as well as from composite rate data, see (.255). (.244) Reaction considered to involve three consecutive steps with (.245) as the rate determining step followed by much more rapid elimination of second and third HCl. (.245) Considered to be the rate determining step for reaction (.244). (.246)-(.252) Authors show that elimination proceeds in four possible ways, trans 1-2, trans 1-4, cis 1-2 and cis 1-4 arranged in order of decreasing ease. Elimination of second HCl considered to be rapid with first step being rate determining. Importance of base illustrated by reactions (.247) and (.248). (.247) Value only approximate for comparison with rate using stronger base NaOH see (.246). (.248) No measurable reaction in 2 hrs. (.254) One of the rate controlling steps in the aromatization of γ-$C_6H_6Cl_6$ see (.240). Rate constant calculated from composite data for consecutive reactions as well as by direct measurement. (.255) One of the rate controlling steps in the aromatization of δ-$C_6H_6Cl_6$ see (.242). Rate constant calculated from composite data for consecutive reactions as well as by direct measurement. (.260) Initial rate, as calculated first order rate constants decreased with progress of reaction. (.263) Calculated second order constants decreased with progress of reaction. Behavior consistent with an assumed mixture of 71% trans- and 29% cis-isomer which reacted 1/85th as fast, see (.262). (.264)(.265)(.266) Calculated first order rate constants decreased with progress of reaction. (.269) (.270) Second order rate constants calculated by dividing pseudo first order constants by concentration of B which was in large excess.

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ELIMINATION
of halogen molecule by halogen ion

Liquid phase

Reaction type: $RCHXCHXR' + X^- \longrightarrow RCH{:}CHR' + X_3^-$
(A) (B) (L) (M)

or $RCHXCHXR' + 3X'^- \longrightarrow RCH{:}CHR + X_3'^- + 2X^-$

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents at end of table.

Rate law is for $-dA/dt$ unless stated otherwise.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.19	.1	$CH_2BrCH_2Br + 3I^- \longrightarrow CH_2{:}CH_2 + I_3^- + 2Br^-$	H_2O	$10^2A = 7-14$; $B = 1$	K^+	= B	k AB	25	2.63	-6				*	(10)
			M 99*	$10^2A \sim 2$; $10B = 1-2$	K^+	= B		30	2.82	-6					(5)
								60	8.34	-5					(5) (7a)
								75	3.72	-4	22.7	7	10		(5) (7a)
			M 72*	$10^2A \sim 2$; $10B = 1-2$	K^+	= B		60	1.13	-4					(5)
			M 63*					30	4.31	-6					
			E 60*			$\mu = 0.22$		40	2.22	-5					
					HCl	$\mu = 0.33$		40	2.16	-5					
					KBr	$\mu = 0.44$		40	2.01	-5					
			C_2H_5OH	$10^2A = 1.5$; $B = 0.3$	Na^+	= B		25	3.40	-6					(4)
								37	1.28	-5					
								56	9.42	-5	21	8	9		(10)
.20		$CH_2BrCH_2I + 2I^- \longrightarrow CH_2{:}CH_2 + I_3^- + Br^-$	Et 5*	$10^2A = 2.5-5$; $B = 0.10$	K^+	= B	k AB	25	6.1	-4				*	(9)
				0.05				35	1.65	-3					
				0.10				35	1.57	-3					
				0.15				35	1.50	-3					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.21		$CH_2ICH_2I + I^- \longrightarrow CH_2{:}CH_2 + I_3^-$	Et 5*	$10^2A = 2\text{-}3.5$;	K^+ or NH_4^+										
				$B = 0.025$	or Na^+	= B	k AB	25	2.26	-3				*	(9)
				0.054				25	2.08	-3					
				0.10				25	1.94	-3					
				0.075				35	5.35	-3					
				0.10				35	4.88	-3					
.22		*trans*-$ICH{:}CHI + I^- \longrightarrow HC{:}CH + I_3^-$	CH_3OH	$10^2A = 2\text{-}6$;			k AB	79	1.83	-6				*	(7)
				$10B = 1\text{-}3.5$				94.5	1.18	-5					
								109	5.07	-5	29.4	4	12		
.23		*cis*-$ICH{:}CHI + I^- \longrightarrow$	CH_3OH	$10^2A = 4$;				140	0					*	(7)
				$B = 0.1$											
.24	.2	$CH_3CHBrCH_2Br + 3I^- \longrightarrow CH_3CH{:}CH_2 + 2Br^- + I_3^-$	M 99*	$10^2A \sim 2$;	K^+	= B	k AB	60	3.11	-6				(7)	(7a)
				$10B = 1\text{-}2.5$				75	1.61	-5	25	9	10		
			M 72*					60	4.67	-6					(7)
			E 68.3*					60	7.25	-6					
			C_2H_5OH	$10^2A = 1.5$;	Na^+	= B		25	4.22	-7					(4)
				$10B = 3$				37	2.12	-6					
								56	2.00	-5	26	3	11		
.25	.10	$CH_3CH_2CH_2CHBrCH_2Br + 3I^- \longrightarrow C_3H_7CH{:}CH_2 + 2Br^- + I_3^-$	C_2H_5OH	$10^2A = 1.5$;	Na^+	= B	k AB	25	3.55	-7				*	(4)
				$10B = 3$				37	2.48	-6					
								56	2.67	-5	27	5	13		
.26	.12	*dl-threo*-$CH_3CH_2CHBrCHBrCH_3 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	k AB	60	1.86	-6				*	(14)
				$10B \sim 2$				75	9.95	-6	26	1	11		

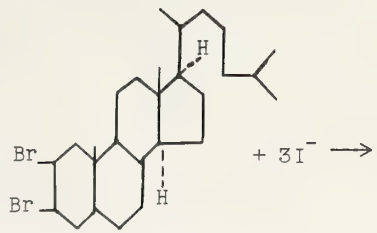
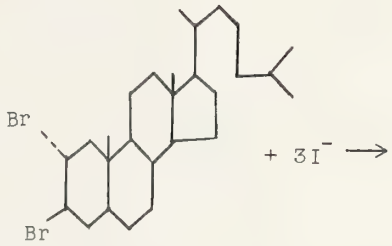
No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.27	.12	*dl-erythro*-$CH_3CH_2CHBrCHBrCH_3 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	*k* AB	60	4.96	-6				*	(14)
				10B ~ 2				75	2.63	-5	26	4	11		
.28		*meso*-$C_2H_5CHBrCHBrC_2H_5 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	*k* AB	60	8.35	-6				*	(14)
				10B ~ 2				75	4.29	-5	25	2	11		
.29		*dl*-$C_2H_5CHBrCHBrC_2H_5 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	*k* AB	60	2.18	-6				*	(14)
				10B ~ 2				75	1.23	-5	27	6	11		
.30	.15	*meso*-$C_3H_7CHBrCHBrC_3H_7 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	*k* AB	60	7.68	-6				*	(16)
				10B ~ 2				60	9.81	-6					(14)
								75	3.78	-5					(16)
								75	5.11	-5	25	4	11		(14)
.31	.16	*dl*-$C_3H_7CHBrCHBrC_3H_7 + 3I^- \longrightarrow$	M 99*	$10^2A \sim 2$;	K^+	= B	*k* AB	60	5.70	-6				*	(16)
				10B ~ 2				60	3.43	-6					(14)
								75	2.99	-5	25				(16)
								75	1.68	-5	24	4	10		(14)
.32	.3	$HOCH_2CHBrCH_2Br + 3I^- \longrightarrow$	C_2H_5OH	$10^2A = 1.5$;	Na^+	= B	*k* AB	25	1.55	-7					(4)
				10B = 3				37	9.1	-7					
								56	8.52	-6	25.3	5	12		
.33	.4	$HOOCCHBrCH_2Br + 3I^- \longrightarrow$	H_2O	$10^2A = 2.5$;	K^+	= B	*k* AB	25	5.52	-6				*	(10)
				B = 1.0	HCl	0.25									
				2.0	"	"		25	5.80	-6					(4)
			C_2H_5OH	$10^2A = 1.5$;	Na^+	= B		25	5.98	-6					
				B = 0.3				37	2.40	-5					
								56	1.36	-4	19.8	1.4	9		
			$(CH_3)_2CO$	$10^2A = 1.5$;	Na^+	= B		0	8.1	-5					
				B = 0.3				25	1.73	-3	19.5	3	11		

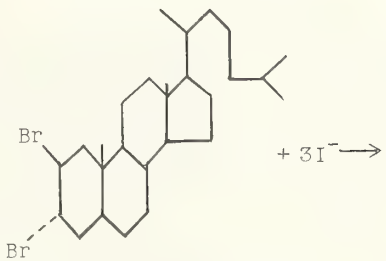
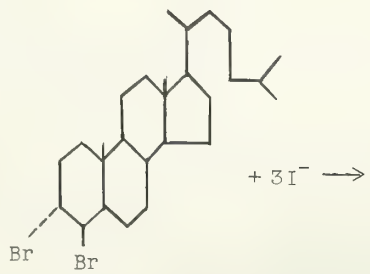
No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.34		$NaOOCCHBrCH_2Br + 3I^- \longrightarrow$	H_2O	$10^2A = 2.5$;											
				$B = 1.0$	K^+	= B	k AB	25	7.29	-7				*	([10])
				2.0	"	"		25	1.16	-6					
				1.0	KBr	1.0		25	1.21	-6					
				1.0	KCl	1.0		25	1.25	-6					
				1.0	$CuCl_2$	0.5		25	1.27	-6					
				1.0	Na^+	= B		25	7.56	-7					
				2.0	"	"		25	8.43	-7					
				1.0	NaBr	1.0		25	1.02	-6					
				1.0	NaCl	1.0		25	1.04	-6					
.35		$HOOCCHBrCHBrCH_3 + 3I^- \longrightarrow$	C_2H_5OH	$10^2A = 1.5$;	Na^+	= B	k AB	37	6.75	-6					([4])
				$B = 0.3$				56	3.27	-5	18	3	7		
.36	.8	*meso*-$HOOCCHBrCHBrCOOH + 3I^- \longrightarrow$	C_2H_5OH	$10^2A = 1.5$;	Na^+	= B	k AB	25	1.80	-5					([4])
				$B = 0.3$				37	5.98	-5					
								56	3.72	-4	19.2	4	9		
.37		$C_2H_5OOCCHBrCH_2Br + 3I^- \longrightarrow$	C_2H_5OH	$10^2A = 1.5$;	Na^+	= B	k AB	25	1.92	-5					([4])
				$B = 0.3$				37	6.88	-5					
								56	3.43	-4	18.2	3	8		
Aryl-substituted alkyl di-halides															
.38	.17	$C_6H_5CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$;	K^+	= B	k AB	40	1.61	-5	21.7	2	10		([8])
				$B = 0.25$											
.39		2-$CH_3C_6H_4CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$;	K^+	= B	k AB	40	4.83	-4					([8])
				$B = 0.25$											

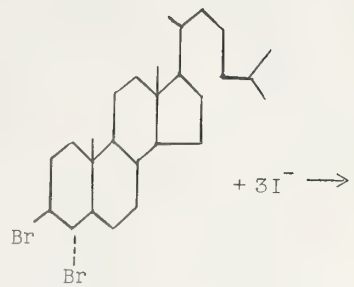
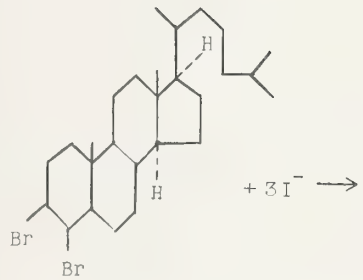
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.40	$3\text{-}CH_3C_6H_4CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	2.42	-5					(8)
.41	$4\text{-}CH_3C_6H_4CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	8.31	-5					(8)
.42	$2,4\text{-}(CH_3)_2C_6H_3CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	2.12	-3					(8)
.43	$2,5\text{-}(CH_3)_2C_6H_3CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	6.55	-4					(8)
.44	$2,6\text{-}(CH_3)_2C_6H_3CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	4.07	-4					(8)
.45	$3,5\text{-}(CH_3)_2C_6H_3CHBrCH_2Br + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	k AB	40	3.39	-5					(8)
.46	$C_6H_5CHBrCHBrC{:}OCH_3 + 3I^- \longrightarrow$	$(CH_3)_2CO$	$10^2A = 1.5$; $B = 0.3$	Na^+	= B	k AB	25	2.07	-3					(4)
.47	$C_6H_5CHBrCHBrC{:}OC_6H_5 + 3I^- \longrightarrow$	$(CH_3)_2CO$	$10^2A = 1.5$; $B = 0.3$	Na^+	= B	k AB	0	1.95	-4					(4)
							9	5.32	-4					
							14	9.9	-4	18	2	11		
.48	$4\text{-}NO_2C_6H_4CHBrCHBrC{:}OC_6H_5 + 3I^- \longrightarrow$	$(CH_3)_2CO$	$10^2A = 1.5$; $B = 0.3$	Na^+	= B	k AB	0	2.91	-4					(4)
							9	8.52	-4					
							14	1.66	-3	19.2	6	12		
.49	$3\text{-}ClC_6H_4CHBrCHBrC{:}OC_6H_5 + 3I^- \longrightarrow$	$(CH_3)_2CO$	$10^2A = 1.5$; $B = 0.3$	Na^+	= B	k AB	14	1.52	-3					(4)
.50	$4\text{-}NaSO_3C_6H_4CHBrCHBrCOOH + 3I^- \longrightarrow$	H_2O	$10^2A = 2.5$; $B = 1.0$	K^+	= B	k AB	25	9.12	-5				*	(10)
			2.0	HCl	0.25		25	9.82	-5					

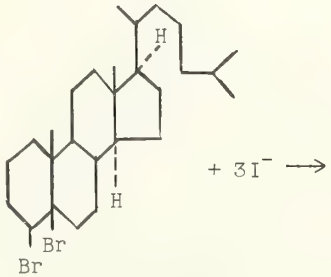
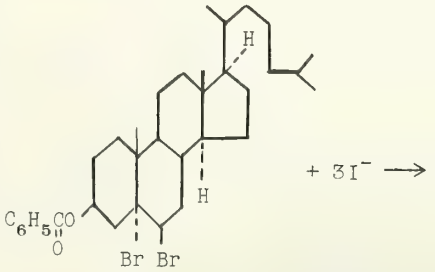
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.51	$4\text{-}NaSO_3C_6H_4CHBrCHBrCOONa + 3I^- \longrightarrow$	H_2O	$10^2A = 2.5$; B = 1.0	K^+	= B	k AB	25	1.83	-5				*	(10)
			2.0	"	"		25	2.45	-5					
			1.0	+KBr	1.0		25	2.52	-5					
			1.0	+KCl	1.0		25	2.58	-5					
			1.0	$+CaCl_2$	0.5		25	2.84	-5					
			1.0	Na^+	= B		25	1.71	-5					
			2.0	"	"		25	2.24	-5					
			1.0	+NaBr	1.0		25	2.31	-5					
	Cyclo-alkyl di-halides													
.52	*trans*-$\overline{CH_2CH_2CHBrCHBr} + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; B = 0.25	K^+	= B	k AB	110	4.5	-7				*	(11)
.53	*trans*-$\overline{CH_2CH_2CH_2CHBrCHBr} + 3I^- \longrightarrow$	M 99*	$10^2A = 2.5$; B = 0.25			k AB	75	2.88	-5				(11) (12)	
							95	1.97	-4				(11)	
							110	7.18	-4	23.2	1.2	10		
.54	*cis*-$\overline{CH_2(CH_2)_3CHClCHCl} + 3I^- \longrightarrow$	M 99*	$10^2A \sim 3$; B = 0.26	K^+	= B	k AB	100	< 2	-7				*	(6)
.55	*trans*-$\overline{CH_2(CH_2)_3CHClCHCl} + 3I^- \longrightarrow$	M 99*	$10^2A \sim 3$; B = 0.26	K^+	= B	k AB	100	< 2	-7				*	(6)
.56	*cis*-$\overline{CH_2(CH_2)_3CHClCHBr} + 3I^- \longrightarrow$	M 99*	10^2A = 2.5-3.3; B = 0.26	K^+	= B	k AB	80	3.80	-7				*	(6)
							100	2.75	-6	25.4	2	9		
.57	*trans*-$\overline{CH_2(CH_2)_3CHClCHBr} + 3I^- \longrightarrow$	M 99*	10^2A = 2.5-3.3; B = 0.26	K^+	= B	k AB	80	3.05	-7				*	(6)
							100	2.48	-6	26.9	1.4	10		
.58	*cis*-$\overline{CH_2(CH_2)_3CHBrCHBr} + 3I^- \longrightarrow$	M 99*	10^2A = 2.5-3.3; B = 0.26	K^+	= B	k AB	80	9.51	-7				*	(6)
							100	6.85	-6	25.4	5	9		

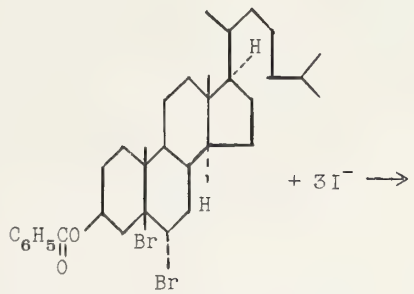
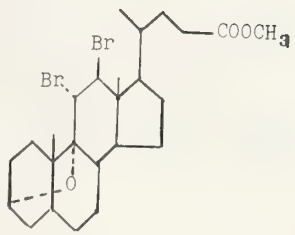
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.59	*trans*-$\overline{CH_2(CH_2)_3CHBrCHBr}$ + $3I^-$ ⟶	M99*	$10^2A = 2.5$; $B = 0.25$	K^+	= B	*k* AB	75	6.27	-6				(11) (12) (13)	
			"				80	1.10	-5				*	(6)
			"				95	4.32	-5					(11)
			"				100	8.16	-5					(6)
			0.13				100	8.5	-5					
			0.25				110	1.86	-4	25.1	4	10		(11)
		CH_3OH	"				100	7.77	-5					(6)
		M99.5*	"				100	7.90	-5					
		M98*	"				100	8.56	-5					
		n-C_3H_7OH	$10^2A = 2$-3; $B = 0.2$-0.5	Na^+	= B	*k* AB	62	1.48	-6				*	(3)
							74	5.93	-6					
							88	2.34	-5	25.9	1.2	11		
.60	*trans*-$\overline{CH_2(CH_2)_4CHBrCHBr}$ + $3I^-$ ⟶	M99*	$10^2A = 2.5$; $B = 0.25$			*k* AB	75	1.35	-4				*	(11)
							95	7.79	-4					
							110	2.88	-3	23.1	4	10		
.61	*trans*-$\overline{CH_2(CH_2)_5CHBrCHBr}$ + $3I^-$ ⟶	M99*	$10^2A = 2.5$; $B = 0.25$			*k* AB	75	2.53	-5				*	(11)
							110	5.25	-4	23	6	9		
.62	*cis*-$\overline{CH{:}CHCHBrCH_2}CHBr$ + $3I^-$ ⟶ $\overline{CH{:}CHCH{:}CHCH_2}$ + I_3^- + $2Br^-$	$CH_3COOC_2H_5$	$10^2A = 6$; $10^3B = 10$	Na^+	= B	*k* AB	24	8.88	-3					(15)
			9.7				24	9.58	-3					
			6.9				24	1.04	-2					
			5.0				24	1.20	-2					
.63	*trans*-$\overline{CH_2CH{:}CHCHBrCHBr}$ + $3I^-$ ⟶ $\overline{CH_2CH{:}CHCH{:}CH}$ + I_3^- + $2Br^-$	$CH_3COOC_2H_5$	$10^2A = 6$; $10^2B = 1$	Na^+	= B	*k* AB	24	7.38	-3					(15)

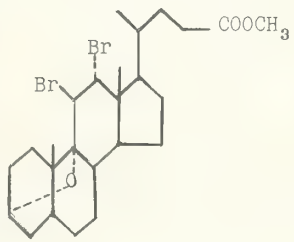
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Poly-cyclic di-bromides													
.64	 (cholest-2-ene dibromide)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B		~20 ~20 ~20	% reacted 3.4 22.5 46.6		time (secs) 5.4×10^4 1.0×10^7 1.9×10^7			*	([2])
.65	 (2α, 3β-dibromocholestane)	$(CH_3)_2CO$	$10^3A = 5$; $10^2B \sim 7$	Na^+	= B		~20	0		5.1×10^6			*	([1])

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
							% reacted		time (secs)			
.66	 (2β, 3α-dibromocholestane)	$(CH_3)_2CO$	$10^3A = 5$; $10^2B \sim 7$	Na^+	= B	~20	7		2.6×10^5		*	(1)
						"	14		8.6×10^5			
						"	43		2.2×10^6			
						"	77		5.1×10^6			
.67	 (3α, 4β-dibromocholestane)	$(CH_3)_2CO$	$10^3A = 5$; $10^2B \sim 7$	Na^+	= B	~20	10		1.7×10^5		*	(1)
						"	21		3.4×10^5			
						"	91		1.2×10^6			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
							k^o	n		A^o	n	
							% reacted		time (secs)			
.68	 (3β, 4α-dibromocholestane)	$(CH_3)_2CO$	$10^3A = 5$; $10^2B \sim 7$	Na^+	= B	~20	1		1.2×10^6	*		(1)
.69	 (cholest-3-ene dibromide)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B	~20	0.1		1.9×10^7	*		(2)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
							% reacted		time (secs)			
.70	 (cholest-4-ene dibromide)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B	~20 "	79.7 100		900 5.4×10^4		*	(2)
.71	 (5α, 6β-dibromocholestan-3β-yl benzoate)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B	~20 "	30.1 69.8		900 1.35×10^4		*	(2)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
							% reacted		time(secs)			
.72	 (5β, 6α-dibromocholestan-3β-yl benzoate)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B	~20	6.3		5.4×10^4		*	(2)
.73	 (methyl 11α,12β-dibromo-3α,9α-epoxy cholanate)	$(CH_3)_2CO$	$10^3A = 3$; $10^2B = 6.7$	K^+	= B	~20	0		1.9×10^7		*	(2)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Literature
							% reacted		time (secs)			
.74	 (methyl 11β, 12α-dibromo-3α, 9α-epoxycholanate)	$(CH_3)_2CO$	$10^3A=3$; $10^2B=6.7$	K^+	= B	~20	12.6		1.35×10^4		*	(2)
						"	53.1		1.91×10^5			
						"	93.7		1.04×10^7			

CODED SOLVENTS

M99* (99.5) (98) (72) (68.3) (63) (60)	Methanol wt. % indicated with H_2O.
E60* (68.3)	Ethanol wt. % indicated with H_2O.
Et5*	Ethanol 5 volumes + H_2O 2 volumes.

COMMENTS

Reaction: (.19) Rate constant calculated by ([10]) based on assumed rate law kAB^2 but converted to kAB which was shown to be rate law by ([5]). (.20)(.21) Rate constants converted to seconds from original minutes and base e from base 10 logarithms. Second order constants calculated by dividing pseudo first order constants by concentration of B. (.22) Values of rate constant extrapolated to zero ionic strength. For reverse reaction see 622.477.85. (.23) No measurable reaction in 22 hours. (.24) By variation of initial concentration ([7]) confirmed reaction order as second order and the stoichiometry involving 3 molecules of B for 1 of A. Recalculated earlier work of ([10]). Second order rate constants of ([4]) observed to decrease with course of reaction. (.25) Calculated second order rate constants observed to decrease with course of reaction. (.26)(.27)(.28)(.29) Rate constants corrected for solvent expansion and empirically determined salt effect. (.30)(.31) Rate constants of both authors corrected for solvent expansion and empirically determined salt effect. Reason for difference between values not apparent. (.33)(.34)(.50)(.51) Data of ([10]) recalculated to stoichiometry involving $3I^-$ and second order rate law by editor. (.52) Rate constant not corrected for thermal expansion of solvent. (.54)(.55) Rate constant limit based upon 1% reaction. (.56) Rate constant calculated for first 30% reaction as calculated values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.11. (.57) Rate constants calculated for first 30% reaction since calculated values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.22. (.58) Rate constants calculated for first 30% reaction since calculated values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.08. (.59) Rate constants calculated for first 30% reaction by ([6]) and up to 20-60% by ([3]) as both found calculated values decreased with progress of reaction. ([3]) found his initial rates to be independent of variation in initial concentrations of both A and B. ([6]) attributed decrease in rate constant to be partially due to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.006. (.60) $\Delta H^{\ddagger}$ = 22.5 of authors converted to E by adding RT. (.61) Rate constant at 110° not corrected for solvent expansion. (.64)(.65)(.66)(.67)(.68)(.69)(.70)(.71)(.72)(.73)(.74) Data gives only order of magnitude of reaction velocity at room temperature. Probably second order rate law but accuracy not sufficient to warrant calculation.

LITERATURE

(1) G.H. Alt, D.H.R. Barton, *CSL* **1954,** 4284. (2) D.H.R. Barton, W.J. Rosenfelder, *CSL* **1951,** 1048. (3) S.J. Cristol, J.Q. Weber, M.C. Brindell, *ACS* 1956, **78,** 598. (4) T.L. Davis, R. Heggie, *J.O.C.* 1937, **2,** 470. (5) R.T. Dillon, *ACS* 1932, **54,** 952. (6) H.L. Goering, H.H. Espy, *ACS* 1955, **77,** 5023. (7) S.I. Miller, R.M. Noyes, *ACS* 1952, **74,** 3403. (7a) D. Pressman, W.G. Young, *ACS* 1944, **66,** 705. (8) L.H. Schwartzman, B.B. Corson, *ACS* 1956, **78,** 322. (9) A. Slator, *CSL* 1904, **85,** 1697. (10) C.F. van Duin, *R.T.C.* 1924, **43,** 341.

(11) J. Weinstock, S.N. Lewis, F.G. Bordwell, *ACS* 1956, **78,** 6072. (12) J. Weinstock, R.G. Pearson, F.G. Bordwell, *ACS* 1954, **76,** 4748. (13) S. Winstein, *ACS* 1942, **64,** 2792. (14) W.G. Young, S.J. Cristol, T. Skei, *ACS* 1943, **65,** 2099. (15) W.G. Young, H.K. Hall, S. Winstein, *ACS* 1956, **78,** 4338. (16) W.G. Young, D. Pressman, C.D. Coryell, *ACS* 1939, **61,** 1640.

ELIMINATION

Ring closure by elimination of $CO_3^{=}$

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments
							k^o	n		A^o	n	
.1	$NaOOCCH_2CH_2CH_2CH_2COONa \longrightarrow \overline{CH_2CH_2CH_2CH_2C}:O + Na_2CO_3$	softened A	M	0-10%	kA; $k = k_o + k_c$	430	$k = 2.7$	-5				*
						440	$k^o = 2.2$	-4				
						449	$k^o = 6.5$	-4				
						464	$k^o_o = 1.16$	-3				
						440	$k_c = 6.5$	-4				
						449	$k^c = 1.18$	-3				
						464	$k^c_c = 2.5$	-3	59	1	15	
.2	$NaOOCCH_2CH_2CH_2CH(CH_3)COONa \longrightarrow \overline{CH_2CH_2CH_2CH(CH_3)C}:O + Na_2CO_3$	Molten A			kA	405	1.87	-4				
						410	2.78	-4				
						415	3.93	-4				
						419	5.25	-4	68	2	18	
.3	$NaOOCCH_2CH_2CH(CH_3)CH_2COONa \longrightarrow \overline{CH_2CH_2CH(CH_3)CH_2C}:O + Na_2CO_3$	Molten A			kA	395	1.77	-4				*
						410	4.82	-4				
			M	0-10%		427	1.38	-3				
			carbon	11%		427	2.1	-3	59	4	15	

COMMENTS

Reaction: **(.1)** Reaction autocatalytic and could be expressed as the sum of two first order rate constants one uncatalyzed and the other catalyzed by carbon. In presence of excess carbon simple first order behavior with rate constant k_c. Reaction rate found to be independent of surface of vessel. Materials tried were silica, platinum and pyrex. **(.3)** Reaction shows only slight catalysis by carbon compared to reaction (.1).

LITERATURE

R.T. Reed, N.B. Thornley, *CSL* **1957**, 3714.

ELIMINATION

Ring-closure with elimination of ROH

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Coded solvents at end of Table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	*cis*-$CH_3C(=CH_3)$-COOH, COOH $\longrightarrow$ CH_3-C-C=O, CH_3-C-C=O (cyclic) + H_2O	$(C_2H_5)_2O$	$10^2A = 3.1$			kA^2	0	1.80	-4				*	([2])
							20	1.41	-3					
							40	8.2	-3					
							60	4.35	-2	16.5	2.8	9		
		E50B*					0	5.66	-4					
							20	3.86	-3					
							40	2.32	-2					
							60	1.09	-1	16.2	5	9		
		E75B*					20	1.12	-2					
		E90B*					20	4.95	-2					
							40	2.77	-1	16	3	10		
		E95B*					20	1.60	-1					
							40	6.63	-1	13	7	8		
		E98.5B*					20	4.83	-1					
							40	1.68	0	11	1.5	8		
		E99.6B*					20	1.13	0					
							40	3.24	0	12	2	7		
		E99.9B*					20	2.00	0					
		Dioxane					20	2.42	-4					
		D98B*					20	3.04	-1					
		$(CH_3)_2CO$					20	6.5	-4					
		H_2O				k_1A	0	1.22	-3					
							0	2.03	-4					
							20	1.52	-3	16	1.3	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	*cis*-CH_3CCOOH ‖ CH_3CCOOH ⟶ *(continued)*	A 10 W*			$k_1A + k_2A^2$		20	k_1=3.8	-5				*	([2])
							20	k_2=1.77	-3					
		A 1 W*				k_2A^2	20	6.52	-4					
.2	$(CH_3)_2C(CH_2COOH)(CH_2C{:}OCH_3) \longrightarrow (CH_3)_2C(CH_2C{:}O)_2CH_2 + H_2O$	H_2O	$10^2A \simeq 2$	H_2SO_4	wt. % 50.6	kA	100	8.87	-6				*	([1])
					50.6		111	2.18	-5					
					50.6		117	3.86	-5					
					50.6		129	1.52	-4	24	1	9		
					59.0		100	2.25	-5					
					64.6		100	4.91	-5					
					72.3		100	9.13	-5					
					72.3		111	2.20	-4					
					72.3		117	3.76	-4					
					72.3		129	1.01	-3	23	5	9		
					86.4		100	1.46	-4					
					91.6		100	2.23	-4					
		CH_3COOH		H_2SO_4	8.94		87	9.86	-6					([4])
					8.94		100	2.32	-5					
					8.94		110	4.62	-5					
			wt. % M=.22		10.05		87	1.22	-5					
			.0		10.05		100	2.47	-5					
			.22		10.05		100	2.96	-5					
			.72		10.05		100	2.71	-5					
			.22		10.05		110	5.82	-5					
.3	$C_2H_5C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow CH_3CHC{:}OCH_2C(CH_3)_2CH_2C{:}O + H_2O$	H_2O		H_2SO_4	wt. % 44.8	kA	88	6.30	-5					([4])
					44.8		101	1.86	-4		$\Delta S^{\ddagger}$=-18.6			
					44.8		110	3.78	-4	22.2	1.7	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
					wt. %									
.3	$C_2H_5C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow$ *(continued)*	H_2O		H_2SO_4	50.7	kA	88	1.20	-4					([4])
					50.7		100	3.14	-4			$\Delta S^{\ddagger}=-19.4$		
					50.7		110	6.65	-4	21.6	1.4	9		
					61.0		79	2.06	-4					
					61.0		87	3.82	-4			$\Delta S^{\ddagger}=-20.6$		
					61.0		100	1.05	-3	20.0	5	8		
		CH_3COOH		H_2SO_4	5.47		81	5.50	-5					
					5.47		88	7.91	-5					
					5.47		100	1.29	-4					
			wt. % M=0.13		4.92		81	4.96	-5					
			0.13		4.92		87	7.33	-5					
			0.0		4.92		100	9.0	-5					
			0.13		4.92		100	1.50	-4					
			0.40		4.92		100	1.59	-4					
			0.80		4.92		100	1.42	-4					
					wt. %									
.4	$n\text{-}C_3H_7C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow$ $C_2H_5\overline{CHC{:}OCH_2C(CH_3)_2CH_2C}{:}O + H_2O$	H_2O		H_2SO_4	42.8	kA	88	1.33	-5					([4])
					42.8		100	3.88	-5			$\Delta S^{\ddagger}=-19.8$		
					42.8		109	8.31	-5	22.8	9	8		
					50.7		87	3.60	-5					
					50.7		101	1.10	-4			$\Delta S^{\ddagger}=-20.3$		
					50.7		117	3.70	-4	22.0	8	8		
					61.0		80	8.34	-5					
					61.0		87	1.38	-4			$\Delta S^{\ddagger}=-20.6$		
					61.0		100	3.90	-4	20.7	5	8		
					65.4		79	1.35	-4					
					65.4		86	2.46	-4					
					65.4		99	6.72	-4	20.9	1.3	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
					wt. %									
.4	$n\text{-}C_3H_7C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow$ *(continued)*	H_2O		H_2SO_4	72.5	kA	81	3.50	-4					(4)
					72.5		86	5.60	-4			$\Delta S^{\ddagger}=-20.5$		
					72.5		99	1.42	-3	19.9	7	8		
					79.5		64	1.40	-4					
					79.5		80	5.62	-4					
					79.5		86	8.64	-4	20.2	1.8	9		
					wt. %									
.5	$n\text{-}C_4H_9C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow$ $n\text{-}C_3H_7\overline{CHC{:}OCH_2C(CH_3)_2CH_2C}{:}O + H_2O$	H_2O		H_2SO_4	50.7	kA	86	4.43	-5					(4)
					50.7		100	1.27	-4			$\Delta S^{\ddagger}=-21.5$		
					50.7		109	2.65	-4	21.4	5	8		
					65.4		80	1.81	-4					
					65.4		87	3.08	-4			$\Delta S^{\ddagger}=-21.7$		
					65.4		100	8.09	-4	19.8	4	8		
					72.1		80	3.82	-4					
					72.1		86	6.77	-4			$\Delta S^{\ddagger}=-20.9$		
					72.1		97	1.43	-3	19.8	8	8		
					wt. %									
.6	$(CH_3)_2CHCH_2C{:}OCH_2C(CH_3)_2CH_2COOH \longrightarrow$ $(CH_3)_2CH\overline{CHC{:}OCH_2C(CH_3)_2CH_2C}{:}O + H_2O$	H_2O		H_2SO_4	61.0	kA	100	2.7	-5					(4)
					61.0		110	5.05	-5			$\Delta S^{\ddagger}=-35$		
					61.0		117	7.5	-5	17.3	4	5		
.7	$\begin{matrix} CH_2CH_2COOC_2H_5 \\ \vert \\ CH_2CH_2COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} CH_2CHCOOC_2H_5 \\ / \quad \backslash \\ CH_2CH_2C{:}O \end{matrix} + C_2H_5OH$	C_2H_5OH	A = 0.10	C_2H_5ONa	2.85	kA	35	2.8	-5				*	(3)
			0.11		2.85		40	5.3	-5					
			0.20		2.85		40	5.7	-5					
			0.1		2.85		45	1.07	-4					
			0.1		2.85		50	2.6	-4	24	5	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.8	$CH_2CH_2COOC_2H_5$ / $CH_3CHCH_2COOC_2H_5$ → $CH_2CHCOOC_2H_5$ / $CH_3CHCH_2C{:}O$ + C_2H_5OH	C_2H_5OH	$A \simeq 0.1$	C_2H_5ONa	2.85	kA	45	2.82	-5				*	([3])
.9	$CH_2CH_2COOC_2H_5$ / $CH_2CH(CH_3)COOC_2H_5$ → $CH_2CHCOOC_2H_5$ / $CH_2CH(CH_3)C{:}O$ + C_2H_5OH	C_2H_5OH	$A \simeq 0.1$	C_2H_5ONa	2.85	kA	35 40 45	2.68 3.93 6.38	-5 -5 -5	17	1	9	*	([3])
.10	$CH_2CH_2COOC_2H_5$ / $CH_2CH(C_2H_5)COOC_2H_5$ → $CH_2CHCOOC_2H_5$ / $CH_2CH(C_2H_5)C{:}O$ + C_2H_5OH	C_2H_5OH	$A \simeq 0.1$	C_2H_5ONa	2.85	kA	35 40 45 50	2.20 4.20 7.92 1.17	-5 -5 -5 -4	25	3	14	*	([3])
.11	$CH_2CH_2COOC_2H_5$ / $CH_2CH(i\text{-}C_3H_7)COOC_2H_5$ → $CH_2CHCOOC_2H_5$ / $CH_2CH(i\text{-}C_3H_7)C{:}O$ + C_2H_5OH	C_2H_5OH	$A \simeq 0.1$	C_2H_5ONa	2.85	kA	45	2.10	-5				*	([3])

CODED SOLVENTS

E x B* $(C_2H_5)_2O$ $(100-x)$ vol. + C_6H_6 x vol.

D 98 B* Dioxane 2 vol. + C_6H_6 98 vol.

A x W* $(CH_3)_2CO$ $(100-x)$ vol. + H_2O x vol.

COMMENTS

Reaction. **(.1)** In non-aqueous solvents is second order with respect to A. In aqueous solvent reaction is first order with respect to A and reverse reaction is important, see 632.441. In mixed solvent 90% $(CH_3)_2CO$ and H_2O combined first and second order equation followed. Authors observe that in non-aqueous solutions the second order rate constant varies inversely with the square of the concentration of the oxygen containing solvent component. **(.2)** Selected data. Plot of log k vs. log $[H_2SO_4]$ is linear with slope of 4.6. Rate constants do not correlate with H_o function. **(.7)-(.11)** Rate constants calculated from combined rate constants $k_1 + k_{-1}$ for forward and reverse reaction and equilibrium constants. Units converted to seconds from original minutes.

LITERATURE

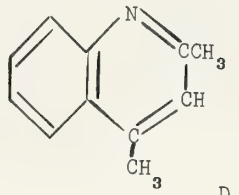
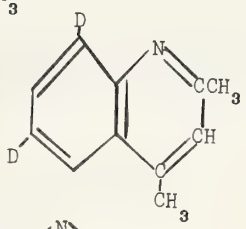
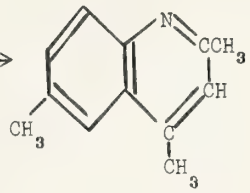
([1]) T. Henshall, W.E. Silbermann, J.B. Webster, *ACS* 1955, **77**, 6656. ([2]) J. Koskikallis, *Acta. Chem. Scand.* 1956, **10**, 882. ([3]) R.I. Reed, M.B. Thornley, *CSL* **1954**, 2148. ([4]) W.E. Silberman, T. Henshall, *ACS* 1957, **79**, 4107.

ELIMINATION

Elimination of H_2O with formation of aromatic ring

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_5N{=}C(CH_3)CH_2C{:}OCH_3 \longrightarrow$  $+ H_2O$	$H_2O + H_2SO_4$ 97.3%	A=0.1			kA	25	3.50	-4	*	(1) (2)
		95.7					25	2.05	-4		
		93.3					25	1.03	-4		
		91.2					25	5.70	-5		
		89.2					25	3.52	-5		
		88.6					25	2.75	-5		
.2	$2,4,6\text{-}D_3C_6H_2N{=}C(CH_3)CH_2C{:}OCH_3 \longrightarrow$  $+ HOD$	$H_2O + H_2SO_4$ 95.7%	A=0.1			kA	25	1.35	-4	*	(2)
		89.2					25	2.68	-5		
.3	$4\text{-}CH_3C_6H_4N{=}C(CH_3)CH_2C{:}OCH_3 \longrightarrow$  $+ H_2O$	$H_2O + H_2SO_4$ 95.5%	A=0.1			kA	25	1.41	-3	*	(1)
		93.1					25	7.15	-4		
		91.1					25	3.53	-4		
		89.2					25	2.05	-4		
		87.6					25	1.23	-4		
		86.3					25	6.45	-5		
		84.5					25	3.98	-5		
		$H_2O + [H_2SO_4]$= 14.42		NH_4HSO_4	2.0		25	2.18	-3		
		10.14			4.0		25	9.23	-4		
		7.97			5.0		25	5.23	-4		
		5.80			6.0		25	2.87	-4		
		1.36			8.0		25	4.97	-5		

COMMENTS

Reaction: (.1) Selected data, units converted to seconds from original minutes. Plot of log of rate constant vs. H_0 is linear. (.2) Units converted to seconds from original minutes. (.3) Selected data, units converted to seconds from original minutes. Plot of log of rate constant vs. H_0 is linear for H_2O-H_2SO_4 medium and plot of log of rate constant vs. log $([H_2SO_4]/[HSO_4^-])$ is linear in both media.

LITERATURE

(1) T.G. Bonner, M.P. Thorne, J.M. Wilkins, *CSL* **1955**, 2351. (2) T.G. Bonner, J.M. Wilkins, *CSL* **1955**, 2358.

ELIMINATION

Elimination of NO_3^- with ring closure

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	$\Delta S^{\ddagger}$
.1	$NO_2N{:}C(NH_2)NHCH_2CH_2ONO_2 \longrightarrow NO_2\overline{NCH_2CH_2HN{:}}CNH_2^+ + NO_3^-$	H_2O	10^4A = 5-14	kA	30	1.37	-6				
					40	5.41	-6				
					50	1.94	-5	26	8	12	
.2	$NO_2N{:}C(NH_2)NHCH_2CH_2CH_2ONO_2 \longrightarrow NO_2\overline{NCH_2CH_2CH_2HN{:}}CNH_2^+ + NO_3^-$	H_2O	10^4A = 5-14	kA	40	3.14	-6				
					50	1.11	-5	25	2	12	-5
.3	$NO_2N{:}C(NH_2)NHCH_2CH(CH_3)ONO_2 \longrightarrow NO_2\overline{NCH(CH_3)CH_2HN{:}}CNH_2^+ + NO_3^-$	H_2O	10^4A = 5-14	kA	30	2.68	-7				
					40	1.22	-6				
					50	4.99	-6	29	1.3	14	+4

COMMENTS

Reactions followed by conductimetric method as well as analytically for M. Conductimetric method indicated slightly higher extent of reaction after about 75%. This was attributed to hydrolysis of product and rate constants were corrected for it.

LITERATURE

C. Boyars, W.F. Sager, S. Skolnik, *ACS* 1957, **78**, 4590.

ELIMINATION
with Ring Closure
Elimination of halogen from halo thio ether

Coded solvents at end of Table.

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$CH_3S(CH_2)_5Cl \longrightarrow CH_3{}^{+}\overline{S(CH_2)_4}CH_2 + Cl^-$	An 50*	$10^2A = 1$			kA	80	2.67	-4				*	(2)
.2	$C_6H_5S(CH_2)_4Cl \longrightarrow C_6H_5{}^{+}\overline{S(CH_2)_3}CH_2 + Cl^-$	An 50*	$10^2A = 1$			kA	70 80 90	4.08 1.07 2.68	-4 -3 -3				*	(2)
.3	$C_6H_5S(CH_2)_5Cl \longrightarrow C_6H_5{}^{+}\overline{S(CH_2)_4}CH_2 + Cl^-$	An 50*	$10^2A = 1$			kA	80 90	1.40 3.58	-5 -5				*	(2)
.4	$^{=}SO_3PCH_2CH_2SCH_2CH_2Cl \longrightarrow {}^{=}SO_3PCH_2CH_2{}^{+}\overline{SCH_2}CH_2 + Cl^-$	An 5*				kA	25	1.2	-2				*	(1)

CODED SOLVENTS

An 50* (5) $(CH_3)_2C{:}O$ % indicated and H_2O (wt. or vol. % not indicated)

COMMENTS

Reaction: **(.1) (.2) (.3)** Reverse reaction negligible. Units converted to seconds from original minutes. **(.4)** Value of rate constant derived from first stage hydrolytic reaction, 212.471(.421), of "mustard", $S(CH_2CH_2Cl)_2$ with added thiophosphate. Units converted to seconds from original minutes.

LITERATURE

(1) P.D. Bartlett, C.G. Swain, *ACS* 1949, **71**, 1406. (2) G.M. Bennett, F. Heathcoat, A.N. Mosses, *CSL* **1929**, 2567.

ELIMINATION
Vth Group Element
Elimination of Carbonium ion from Quaternary ammonium salt

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$C_6H_5N(CH_3)_3^+ + CH_3O^- \longrightarrow C_6H_5N(CH_3)_2 + (CH_3)_2O$	CH_3OH	$10^2A \sim 2$; $10^2B \sim 4$	I^-	= A	kAB	69.8	9.71	-5			
				Na^+	= B		80.9	4.39	-4			
							95.3	2.69	-3	32.7	7	16
.2	$p\text{-}CH_3C_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow p\text{-}CH_3C_6H_4N(CH_3)_2 + (CH_3)_2O$	CH_3OH	$10^2A \sim 2$; $10^2B \sim 4$	I^-	= A	kAB	69.7	5.66	-5			
				Na^+	= B		80.9	2.67	-4			
							95.2	1.68	-3	33.3	1.0	17
.3	$o\text{-}FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow o\text{-}FC_6H_4N(CH_3)_2 + (CH_3)_2O$	CH_3OH	$10^2A \sim 2$; $10^2B \sim 4$	I^-	= A	kAB	58.4	2.77	-4			
				Na^+	= B		69.6	1.28	-3			
							80.6	5.14	-3			
							90.8	1.72	-2	30.5	4	16
.4	$m\text{-}FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow m\text{-}FC_6H_4N(CH_3)_2 + (CH_3)_2O$	CH_3OH	$10^2A \sim 2$; $10^2B \sim 4$	I^-	= A	kAB	58.3	7.80	-5			
				Na^+	= B		69.2	3.59	-4			
			2 4				80.9	1.71	-3			
			4 2				80.9	1.71	-3			
			4.1 4.1				80.9	1.38	-3			
			3.7 8.0				80.9	1.25	-3			
			~2 ~4				91.4	6.22	-3	31.8	7	16
.5	$p\text{-}FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow p\text{-}FC_6H_4N(CH_3)_2 + (CH_3)_2O$	CH_3OH	$10^2A \sim 2$; $10^2B \sim 4$	I^-	= A	kAB	58.6	3.44	-5			
				Na^+	= B		68.9	1.52	-4			
							80.7	7.50	-4			
							91.9	3.13	-3	32.6	9	16

LITERATURE

W.L. Bevan, G.C. Bye, *CSL* **1957**, 3194.

ELIMINATION FROM FUNCTIONAL GROUP

N_2O from aci form of nitro alkane

Reaction type: $2\,R_1R_2CNO_2^- + 2\,H^+ \longrightarrow 2\,R_1R_2C{:}O + N_2O + H_2O$

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
.1	$2\,(CH_3)_2CNO_2^- + 2H^+ \longrightarrow 2\,(CH_3)_2C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 7$; $10^2B = 2\text{-}10$	$-dA/dt = k\,AB$	0	1.30	-2	
.2	$2\,\overline{CH_2CH_2CH_2}CNO_2^- + 2H^+ \longrightarrow 2\,\overline{CH_2CH_2CH_2}C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 7$; $10^3B = 3\text{-}20$	$-dA/dt = k\,AB$	0	1.3	-1	*
.3	$2\,\overline{CH_2(CH_2)_3}CNO_2^- + 2H^+ \longrightarrow 2\,\overline{CH_2(CH_2)_3}C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 6$; $10^2B = 4\text{-}20$	$-dA/dt = k\,AB$	0	5.3	-3	
.4	$2\,\overline{CH_2CH_2CH}(CH_3)CNO_2^- + 2H^+ \longrightarrow 2\,\overline{CH_2CH_2CH}(CH_3)C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 6$; $10B = 1\text{-}5$	$-dA/dt = k\,AB$	0	4.5	-3	
.5	$2\,\overline{CH_2(CH_2)_4}CNO_2^- + 2H^+ \longrightarrow 2\,\overline{CH_2(CH_2)_4}C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 5$; $10^3B = 3\text{-}40$	$-dA/dt = k\,AB$	0	1.48	-1	
.6	$2\,\overline{CH_2(CH_2)_5}CNO_2^- + 2H^+ \longrightarrow 2\,\overline{CH_2(CH_2)_5}C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 5$; $10^2B = 5\text{-}20$	$-dA/dt = k\,AB$	0	2.3	-3	
.7	$2\,[\overline{CH_2CH_2CH}]_2CNO_2^- + 2H^+ \longrightarrow 2\,[\overline{CH_2CH_2CH}]_2C{:}O + N_2O + H_2O$	80 vol % $CH_3OH + H_2O$	$10^4A \sim 5$; $10B = 1\text{-}3$	$-dA/dt = k\,AB$	0	3.0	-3	

COMMENTS

General. Aci form of nitro alkane produced by addition of alkali prior to reaction. Pseudo first order rate constants converted to second order constants by dividing by concentration of excess acid added at start of reaction.

Reaction. (.2) In doubt as products other than cyclobutanone observed.

LITERATURE

M. F. Hawthorne, *ACS* 1957, **79**, 2510.

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